Research progress of perovskite materials as catalysts

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Abstract. Perovskite-type materials have become a research hotspot in the field of materials science due to their excellent structural stability and physicochemical properties. This paper briefly reviews the preparation methods of perovskite materials and their use as catalysts.

1. Introduction

Typical perovskite metal oxides have a general structure of ABO₃, where A is a metal ion with a large ionic radius, located in the center of the cubic structure of the perovskite crystal, and coordinated with 12 O; B is a metal ion with a small ionic radius located at the apex angle of the cubic structure of the perovskite crystal, and 6 O coordination. Theoretically, if the radius of the A, B, and O ions meets the structural tolerance factor \( t = \left( \frac{r_A + r_B}{r_B + r_O} \right) \), typical perovskite crystal structure can be stable (Figure 1 (a)). The ideal perovskite is a cubic structure with a Pm3m-O1h space group. The atoms in the structure space alternate with each other. The length of the B-O bond is equal to 1/2 of the cubic unit cell. At the same time, the A-O bond length is \( \sqrt{2} \) times the cubic cell parameter[4]. However, since the materials are often unable to perfectly control the preparation conditions during the preparation process, such materials often exhibit lattice distortion or defects in the presence of a perovskite structure, and this material property also becomes the theoretical basis for its application. The broad structural constraints of perovskites \( (t = 0.75 ~ 1) \) allow a variety of elements to meet their structural requirements, making them exhibit good elemental adjustability. Usually, the A site in the perovskite structure plays a structural support role, and the B site is a catalytically active site. The A and B sites have mutual influences and constraints. Of course, ensuring charge balance is also one of the structural stability factors. In general, due to the charge balance constraint, the ideal perovskite crystal composition can be expressed as: \( A^{1+}B^{2+}O^3 \), \( A^{2+}B^{4+}O \) or \( A^{3+}B^{3+}O \). In the process of co-equilibration of elements and charges, a large number of defects, vacancies, and lattice flow phenomena are formed, resulting in such materials exhibiting good superconducting properties, ferromagnetic properties, piezoelectric properties, thermistor properties, and heat, a series of good application properties such as stability.
2. Method for preparing perovskite material

2.1. Coprecipitation
The coprecipitation method is to prepare a superfine powder by precipitating the precursors in a stoichiometric ratio with the components which have been uniformly mixed in the solution, and then calcining and decomposing them to prepare ultrafine powders [5]. Compared with other methods, it has the advantages of lower sintering temperature and shorter sintering time, and the prepared perovskite powder has higher specific surface area and reactivity. However, the impurity ions carried by the precipitant tend to remain in the matrix, which may have a certain influence on the catalytic activity of the catalyst. Therefore, this method still has certain limitations in the improvement of the specific surface area and catalytic performance of the powder, and hard agglomeration is likely to occur during the drying process of the precipitate. Gao Ba et al[5] successfully prepared BaZr\textsubscript{1-x}Y\textsubscript{x}O\textsubscript{3-δ} powder by co-precipitation method, and proved the formation of BaZr\textsubscript{1-x}Y\textsubscript{x}O\textsubscript{3-δ} powder by means of infrared spectroscopy and X-ray diffraction analysis, and BaZr\textsubscript{1-x}Y\textsubscript{x}O\textsubscript{3-δ} powder The conductivity of the body at 800 °C was 1.71*10\textsuperscript{-4} S/cm.

2.2. Sol-gel method
The sol-gel method is a wet chemical method for preparing ultrafine particles. This method generally uses an organometallic alkoxide as a raw material, and obtains a solid precursor by hydrolysis, polymerization, drying, etc., and finally obtains a perovskite-type nanomaterial by appropriate heat treatment [6]. Compared with other methods, the sol-gel method has the advantages of high product purity, uniform particle size, low sintering temperature, easy control of the reaction process, etc., but has the disadvantages of longtime consumption, small processing amount, high cost and insufficient luminous intensity. Sun et al [7] synthesized a La\textsubscript{0.8}Sr\textsubscript{0.2}CoO\textsubscript{3} sample with a rare earth metal La substituted by Sr by sol-gel method. The crystal structure of perovskite was determined by XRD diffraction analysis.

2.3. Hydrothermal
The hydrothermal method is a method of chemical synthesis in a supersaturated aqueous solution of high temperature and high pressure. The powder obtained by this method has high crystallinity, less agglomeration and high sintering activity, and has been widely recognized by people, and is a better method for preparing high specific surface area catalysts. Zhang Yue et al [8] prepared spindle-like, rod-like and short-chain perovskite-type oxidation by hydrothermal method using spindle-shaped single crystal copper oxide, flake single crystal yttrium oxide and nitrate as metal sources. La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{4} (x=0,1) single crystal nano-micron particles, this perovskite material has good catalytic oxidation performance of methane.
2.4. Micro emulsion method

Micro emulsions are dispersion of thermodynamically stable, isotropic, and translucent structures formed from two mutually incompatible liquids. The micro emulsion system is a thermodynamically stable mixed system with the advantages of low synthesis temperature, small particle size and adjustable grain morphology. It is widely used in the synthesis of perovskite materials [9].

3. Catalytic properties of perovskite materials

Perovskite materials are widely used in the field of catalysis due to their unique structural properties and exhibit excellent catalytic properties.

3.1. Photocatalytic performance of perovskite catalysts

Fu Xixian et al. conducted spectral analysis on CaTiO₃, CdTiO₃, PbTiO₃, La-PbTiO₃, LaCrO₃, LaMnO₃, LaFeO₃ and LaCoO₃ perovskite oxides. It was found that the above materials have different degrees of light absorption in the visible region [10]. The study suggests that the catalytic activity of the perovskite photocatalyst is related to the difference in the electronegativity of the B site ion in the structure, and the electronegativity of the divalent ion increases and the polarization of the oxygen atom coordinated with it strengthens. In order to increase the 2p orbital electron cloud deformation of the oxygen atom, the energy required to transfer the charge from 2p to 3d is reduced, and the relatively low energy excitation electron can make it transition from the valence band to the conduction band, thus the photocatalytic activity It will increase accordingly. The research team also conducted photocatalytic studies on doped perovskite materials and compared their catalytic performance. For example, when the LaFeO₃ perovskite is doped with Cu at the B site, the photocatalytic performance of the doped catalyst is better than that of the undoped catalyst. The doping causes the non-stoichiometry of LaFeO₃, and the photocatalytic activity also depends on the doping amount. Increase and increase. When the Cu doping is 5% (LaFe₀.9₅Cu₀.0₅O₃), the photocatalytic effect is the best, and the photogenerated holes diffuse to the surface of the particles at a faster rate, which promotes the conversion of surface-adsorbed oxygen species into high activity free. Base, thereby enhancing photocatalytic activity.

3.2. Oxidation catalytic performance of perovskite catalyst

The perovskite material (Ba₀.₃Mg₀.₃FeO₃) can store NOₙ well. On the one hand, the doping of Mg causes spatial distortion of the perovskite crystal lattice, which promotes the large amount of oxygen vacancies that can be used to store NOₙ. The Mg element, which is free from the crystal of the perovskite crystal, may form a monodentate nitrate with NOₙ in the form of a basic oxide [11]. LaMn₁₋ₓCuₓO₃ doped perovskite has good catalytic activity for the selective catalytic reduction of NO and C₃H₃ under oxygen-free conditions. When Mn is replaced by Cu, excess oxygen is generated in the system, and NO can be absorbed to α. The oxygen species are activated and further promote the reaction when the system x = 0. At 2, the catalytic activity is the highest [12]. The use of oxidation reaction to treat NO, SOₙ and other atmospheric pollutant gases in automobile exhaust gas is also one of the important applications of perovskite materials [13]. Let the noble metal ions become the B-doped element of perovskite, and obtain the expected three-way catalysis, which can reduce the amount of precious metals and obtain good NOₙ and SOₙ treatment effects. For example, Fierro et al. used La₁₋ₓCeₓNiO₃ catalyst for CH₄ reforming reaction to obtain good reaction performance [14].

3.3. Perovskite catalyst for water gas shift reaction performance

The water gas shift reaction is an important hydrogen production reaction (CO(g) + H₂O = CO₂(g) + H₂(g)), through which efficient conversion of toxic and harmful CO energy to clean energy H₂ can be achieved. La₂₋ₓCexCu₁₋ₓZnₓO₄ perovskite has good catalytic activity for water-gas shift reaction at high temperature, when the structure is x = 0, 1, y = 0, its catalytic activity is the best, because the structure (La₁₋₀.₉₅Ce₀.₀₅) CuO₄ and La₂CuO₄ structure exist at the same time, and the specific surface area performance is the best [15]. Ca-doped La₂CuO₄ perovskite catalysts are used in water-gas shift
reactions. When Ca is doped at 5% to 10%, it has the best conversion efficiency, the TOF value is the largest, and the Ca-doped system is larger. The specific surface area and reducibility of Cu0 and Cu + species are the main reasons for their good catalytic activity.

3.4. Perovskite catalysts for the synthesis of higher alcohols
Tien-Thai et al. carried out Fischer-Tropsch synthesis with Co, Cu coexisting doped perovskite catalyst LaCo1-xCuxO3-δ (x = 0, 0.1, 0.2, 0.3, 0.4). The catalyst exhibits good product distribution selectivity properties, where x = 0. At 3 o'clock, its high alcohol selectivity performance is about 36.5% to 49.5%. The Co and Cu elements in the perovskite structure are uniformly distributed and have strong interaction and synergistic effects, which are important reasons for their effective control of product distribution [16].

3.5. Performance of perovskite catalysts for methanol synthesis
Until 2009, Xiamen University, Jia et al. [17] based on previous studies, prepared two types of perovskite catalysts for the study of methanol synthesis by CO2 hydrogenation, and found that LaCr0.5Cu0. The catalyst has a relatively high methanol selectivity under given conditions and its carbon selectivity is up to 90.8%, the medium-strong basic position in the structure is considered to be the active site of the reaction, which plays an important role in the high selectivity of the reaction. In addition, Jia et al. also prepared a LaMn1-xCuxO3 (0 ≤ x < 1) manganese-based copper doped perovskite material and studied the performance of CO2 hydrogenation to methanol [18]. It was found that the Cu element in the system Cu + is dominant, and when x = 0. At 5 o'clock, the catalyst was able to exhibit excellent methanol selectivity, which is consistent with the theoretical assumptions of Bourzutschky et al.

The authors prepared a series of A-doped La0.8M0.2Mn0.5Cu0.5O3 type perovskite catalyst and a series of structural properties and CO2 hydrogenation performance of methanol synthesis [19], the results show that the LaMnO3 perovskite structure is very stable, the reduction process will not destroy its crystal structure, only to a certain extent There is a disturbance in its crystal space structure. In addition, when the A site La is replaced by other elements, the Cu element in the perovskite has a certain degree of overflow, and the defects of the material are more abundant. The doped material has better reduction properties, low temperature hydrogen adsorption performance and moderate alkali strength. The Zn-doped catalyst has the best CO2 hydrogenation to synthesize methanol activity and selectivity.

4. Conclusion
The various preparation methods and wide application fields of perovskite materials have made it a focus of attention. The special structural properties bring about its diverse material properties, which greatly expands the related applications of such materials. Doped perovskites appear to exhibit superior catalytic performance, structural defects, and electronic defects in catalytic applications. In the field of photoelectrochemistry, perovskite materials are widely used as electrode materials, and the effect is good, which has a strong industrialization trend. In the field of catalysis, perovskites can be studied as catalysts for many types of reactions, but due to the significant disadvantages of the perovskite materials having a small specific surface area, they are encountered in the process of industrialization. Therefore, further exploration of new preparation methods to improve the specific surface area of perovskite materials has become a major focus for improving the application of such materials in the field of catalysis. Optimizing the specific surface area of the material and achieving high dispersion of the reaction-related active sites on the large specific surface area is an important way to comprehensively improve the catalytic performance of the perovskite catalyst.

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