



Review

Nanostructured perovskite oxides as promising substitutes of noble metals catalysts for catalytic combustion of methane



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ABSTRACT

Heterogeneous catalytic combustion provides a feasible technique for high efficient methane utilization. Perovskites ABO_3 -type materials have received renewed attention as a potential alternative for noble metals supported catalysts in catalytic methane combustion due to excellent hydrothermal stability and sulfur resistance. Recently, the emergence of nanostructured perovskite oxides (such as three-dimensional ordered nanostructure, nano-array structure) with outstanding catalytic activity has further driven methane catalytic combustion research into spotlight. In this review, we summarize the recent development of nanostructured perovskite oxide catalysts for methane combustion, and shed some light on the rational design of high efficient nanostructured perovskite catalysts *via* lattice oxygen activation, lattice oxygen mobility and materials morphology engineering. The emergent issues needed to be addressed on perovskite catalysts were also proposed.

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1. Introduction

Methane, with abundant reserves on earth, is regarded as the most promising clean fossil energy [1]. In conventional methane combustion processes, the flame temperature can reach up to 1100 °C, which inevitably leads to additional energy waste and produces pollutant gases (such as nitrogen oxides (NO_x), carbon monoxide (CO)) [2]. Recently, the boost of natural gas vehicles also promotes the increased utilization of earth-abundant natural gas energy [3], which leads to a large amount of methane emissions and thus aggravates its environmental burden. Methane emissions from automobile exhaust and coal mine have also contributed to the greenhouse effect and global warming [3,4]. Due to the increasing energy efficiency requirements and stringent environmental emission regulations, improving high utilization efficiency of methane is an urgent issue needed to be addressed.

Heterogeneous catalytic combustion of methane has been reported to be able to improve the energy utilization efficiency of methane and control unnecessary atmospheric pollution [2,5,6]. Supported palladium oxides exhibit outstanding catalytic

performance for methane combustion [7]. However, metal oxide supported PdO catalysts tend to deactivate below 450 °C, which seriously hinders their long-term application in catalytic combustion. It is likely that accumulation of hydroxyls on the supports prevent the migration of oxygen to active Pd sites and thus inhibits the catalytic reaction [8]. Moreover, the high cost of Pd also limits its broad application in methane catalytic combustion and methane emission control [9,10].

Recently, accompanied with the development of nanomaterials synthesis technology, nanostructured perovskite ABO_3 -type materials with increased surface area have received renewed attention as a potential industrial catalyst for exhaust emission control [11]. They were proposed as potential non-precious metal catalysts in methane catalytic combustion due to excellent hydrothermal stability and sulfur resistance compared with Pd-based catalysts. Manganese- and cobalt-based perovskites have been proven to show excellent catalytic activity for oxidation (combustion) reactions [12–14]. The concentration of adsorbed oxygen, the activity of lattice oxygen and redox properties of B-site ions are closely related to the catalytic properties of perovskite oxides. In this review, we have summarized the recent research progress on nanostructured perovskite oxides for catalytic methane combustion as well as the existing issues need to be addressed in the near future.

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2. Mechanism for methane combustion

Significant efforts have been devoted to elucidating the mechanism of methane combustion on different types of catalysts. Breakage of the first C-H bond is regarded as the first and the rate-dependent step for methane catalytic combustion due to its extremely high activation energy (439.3 eV). Noble metals and transition-metal oxides based catalysts have been widely studied for catalytic combustion of methane. Pd based catalysts have been well-studied as high-performance catalysts for CH₄ combustion. Chin and Iglesia *et al.* [15] expounded an explicit mechanistic pathway for C-H bond activation from the perspective of theory and experiment. The catalytic reactivity for C-H bond activation varied with Pd chemical states, O centers involved and surface oxygen coverages. Chemical potential of oxygen was closely related to the extent of C-H bond activation. The higher oxygen chemical potential, the easier C-H bond activation on the catalysts surface.

In addition to noble metal based catalysts, single-metal-oxide-based catalysts (such as copper oxide (CuO) [16] along with MnO_x-based catalysts [17] and spinel [3]) were also investigated as efficient catalysts for methane combustion. Feng *et al.* [16] have first reported the study of the catalytic combustion of methane over CuO nanowires (NWs). The conversion rate of CH₄ over the catalytic CuO NWs was almost 40% at 500 °C and the catalytic activity of the CuO NWs could remain stable for at least 24 h at 500 °C, which proved that CuO NWs have great potential to be effective catalysts for methane combustion. Zhang *et al.* [17] prepared MnO_x-NiO composite oxide catalysts *via* co-precipitation method, which exhibited superior catalytic performance in the lean methane oxidation due to good reducibility and oxygen mobility. Tao *et al.* [3] had observed that NiCo₂O₄ exhibited better catalytic activity than precious metal-catalysts. The CH₄ activation mechanism was also different: CH₄ first dissociated to -CH₃ on metal sites (Ni³⁺), then coupled with a surface lattice oxygen (O²⁻) to form -CH₃O; and it dehydrogenized to -CHO for successive two steps; finally -CHO was converted into CO₂.

Compared with the well-studied CH₄ catalytic oxidation mechanism on NiCo₂O₄, mechanistic understanding of the methane combustion over perovskite-type catalysts is still under debating. Pena and Fierro *et al.* [18] firstly investigated the kinetics of methane catalytic oxidation over perovskites catalysts. Eley Rideal (E-R) mechanism, in which gaseous methane reacted with dissociative adsorbed oxygen species on the perovskite surface, was proposed. Then, Auer and Thyron *et al.* [19] had conducted another detailed kinetic analysis: (1) CH₄ first adsorbed on the catalyst surface to form adsorbed CH_{4(ad)}; (2) Dioxygen fast transformed into active oxygen species O* and O* reacted with CH_{4(ad)} to form intermediate I_s; (3) Finally I_s quickly transformed into adsorbed CO_{2(ad)} and H₂O_(ad), and then CO_{2(ad)} and H₂O_(ad) desorbed to molecular CO₂ and H₂O. The oxidation rate of methane was controlled by desorption of products molecules (CO₂ and H₂O). According to their calculation, the Mars and van Krevelen mechanism (MvK mechanism) was more suitable pathway for methane combustion. The methane oxidation process was mainly dependent on lattice oxygen (O²⁻) in perovskite oxides [20]. Fig. 1 illustrated the methane oxidation process through MvK pathway: (1) The methane in the gas phase first adsorbed on the A site to form CH_{4(ad)}; (2) CH_{4(ad)} was attacked by surface lattice oxygen to form CH₃ and the latter was continuously oxidized by surface lattice oxygen to generate CO_{2(ad)} and H₂O_(ad) with the generation of oxygen vacancies; (3) CO_{2(ad)} and H₂O_(ad) desorbed from the catalysts surface to form molecule CO₂ and H₂O, and lattice oxygen was regenerated by refilling of oxygen vacancies with surface adsorbed oxygen. In addition, the amount of active oxygen species also plays an important role in methane catalytic combustion.

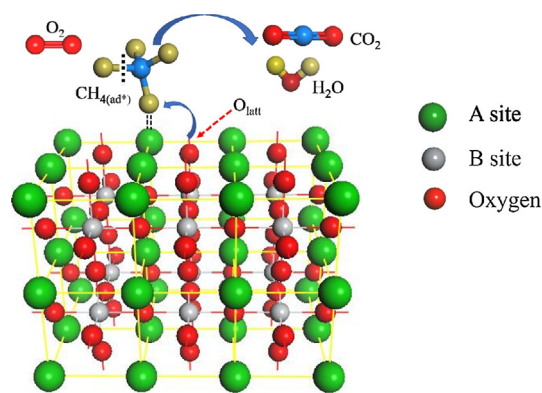


Fig. 1. The pathways of CH₄ combustion on ABO₃-type perovskites following MvK mechanism.

However, further quantitative investigation on each step of MvK mechanism is needed to obtain a perspicuous understanding.

3. Rational design of perovskite oxide catalysts

The typical ABO₃-type perovskite oxides show an ideal cubic structure unit cell with space group Pm3m-O_h in Fig. 2a [21], in which the larger A ion is in dodecahedral coordination with oxygen and the smaller B ion is 6-fold coordinated toward oxygen ion. Due to its stable crystal structure, the A and B cations in perovskites could be partially substituted and give rise to substituted compounds with formula of A_{1-x}A'_xB_{1-x}B'_xO₃ [18]. As shown in Fig. 2b [22], A- or B-site substitution in perovskites has also brought the change of metal ions' oxidation states in the crystal structure and led to the generation of oxygen vacancies. The vast majority of metallic elements from the periodic table could be used as substituted ions, which further gives rise to the great flexibility of perovskites constitutions. The broad family of perovskites oxides also provides the potential for their application in various catalytic processes. Furthermore, the unique structure of perovskite oxides has the possibility to incorporate other types of A or B ions with suitable size and charge, which could change the valence state and nature of lattice ions, thus leading to the tailorable redox and physicochemical properties.

3.1. Design of redox properties

The catalytic activity of perovskite oxides is closely related to their redox properties [23,24]. And the intrinsic redox properties of perovskite oxides are generally determined by B-site cations properties. Temperature-programmed reduction (TPR) is typically used to investigate the redox properties of perovskite oxides. Generally speaking, the lower temperature of the TPR peak, the better reducibility of the perovskite catalyst. As shown in Fig. 3a, selective-dissolution LaMnO₃ sample exhibited the lowest

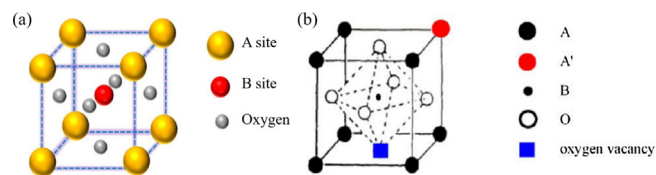


Fig. 2. (a) Schematic illustration of an ideal ABO₃ perovskite unit cell. Copied with permission [21]. Copyright 2015, American Chemical Society. (b) Crystal model of A site doped ABO₃ perovskite with oxygen vacancy. Copied with permission [22]. Copyright 2009, Elsevier B.V.

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