

Article

Study on the Catalytic Reduction Performance of Mg Doped BaSnO₃ Perovskite for CO₂ Conversion

Leyang Guo * and Junwu Guo

Marine Merchant College, Shanghai Maritime University, Shanghai 201306, China; jwguo@shmtu.edu.cn

* Correspondence: 202240110016@stu.shmtu.edu.cn

Abstract

Perovskite possess tunable crystal structures that enable the creation of active sites favorable for CO₂ adsorption and activation through appropriate doping, while their electronic structures facilitate electron transfer during catalytic reactions. In this study, BaSnO₃ was modified by substituting 4% of Ba with Mg to obtain Ba_{0.96}Mg_{0.04}SnO₃ via a co-precipitation method. Structural and physicochemical characterization (ICP, XRD, SEM-EDS, BET) revealed that Mg doping reduced particle size, increased specific surface area by 26%, and enhanced oxygen storage capacity by 6.1%. The doped catalyst also exhibited improved thermal stability, with smaller losses in surface area and oxygen storage after 1200 °C thermal aging. CO₂ adsorption tests showed higher adsorption rates and capacities, while catalytic reduction experiments demonstrated that Mg doping prolonged the catalyst's lifetime from 24 to 40 cycles and increased maximum carbon deposition from 12.68% to 22.54%. These results indicate that Mg doping effectively enhances BaSnO₃'s catalytic activity, structural stability, and durability, making Ba_{0.96}Mg_{0.04}SnO₃ a promising candidate for CO₂ thermal reduction applications.

Keywords: perovskite; performance characterization; doping; oxygen storage capacity; grain refinement

1. Introduction

Reducing CO₂ emissions from marine propulsion remains a critical challenge as shipping moves toward low-carbon operation. Post-combustion carbon capture—including absorption, adsorption, membrane separation, and cryogenic routes—has seen substantial technological progress, yet on-board deployment still faces penalties in footprint, mass, energy demand, and operational complexity, which are especially acute for near-shore and inland vessels with limited capacity and short duty cycles [1–4]. As a complementary strategy, catalytic conversion of CO₂ to elemental carbon has advanced across photocatalytic, electrocatalytic, biocatalytic, and thermal pathways [5]. Fundamentally, activating the linear and thermodynamically stable CO₂ molecule requires tailored electron transfer and reaction environments to lower kinetic barriers and direct selectivity [6]. Among available options, thermal catalytic decomposition of CO₂ to C is attractive for exhaust after-treatment if robust high-temperature catalysts can be developed.

Perovskite was attractive because A/B-site tunability, oxygen-vacancy chemistry, and mobile lattice oxygen jointly governed adsorption/activation and redox cycling under reaction conditions [7,8]. Within this family, BaSnO₃ offered favorable textural features and accessible active sites for surface reactions relevant to CO₂ conversion, as being discussed by Ye et al. [9]. Building on this foundation, Wang et al. demonstrated that A-site substitution



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in $\text{La}_{1-x}\text{K}_x\text{CoO}_3$ enabled highly active soot/ NO_x removal under loose-contact conditions, illustrating how cation choice tunes redox and oxygen mobility in perovskites [7].

Zooming on defect engineering, Balamurugan et al. showed that Fe doping in BaSnO_3 created oxygen vacancies trapping electrons (F-centers), whereas W co-doping donated electrons and suppressed vacancy formation that it was direct evidence that B-site chemistry governed vacancy populations and electronic states in the stannate lattice [10].

In a complementary context, Lee et al. markedly improved reliability for Mg-doped BaTiO_3 during highly accelerated life testing, highlighting the importance of dopant identity and precursor chemistry [11].

Using DFT on iron oxides, Hao et al. found that Mg-doped $\gamma\text{-Fe}_2\text{O}_3$ donated electrons, redistributed surface charge, and modified acidity to facilitate the $\text{NH}_3 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$ route—an example of dopant-controlled reaction pathways [12].

At the scale of double perovskites, Zhong et al. prepared $\text{La}_2\text{NiB}'\text{O}_6$ ($\text{B}' = \text{Co/Mn/Fe}$) and showed that $\text{La}_2\text{NiCoO}_6$ reached 91.3% CO_2 methanation at 400 °C after simple reduction, owing to higher oxygen-vacancy density, better reducibility, and excellent Ni dispersion arising from Ni– B' synergy [13].

These exemplars collectively motivate A-site Mg substitution in BaSnO_3 as a means to enrich oxygen vacancies, modulate redox properties, and stabilize the lattice under high-temperature cycling, thereby improving CO_2 adsorption/activation and durability. In perovskite like catalyst systems, the doping strategy of A-site can effectively regulate the crystal structure, which may be accompanied by the generation of oxygen vacancies, thereby affecting the redox state of active ions occupying B-site. This dynamic regulation helps promote the formation of AO layer and significantly enhance the overall activity of the catalyst. B-site doping, as a key strategy, directly acts on the activation site and adsorption interface to significantly regulate the activity of the catalyst.

Nevertheless, In the above references, Mg-doped BaSnO_3 for CO_2 thermal reduction has not been systematically evaluated. To solve this problem of systematically evaluating the thermal reducibility of Mg-doped BaSnO_3 for CO_2 , the work of this paper tests the hypothesis that 4% A-site Mg substitution in BaSnO_3 , combined with reduction-induced oxygen deficiency to strengthen CO_2 adsorption/activation and durability under high-temperature cycling. Further $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ was synthesized via co-precipitation and its structure–property–performance relationships was assessed through comprehensive physicochemical characterization and CO_2 adsorption/kinetic tests.

2. Preparation of Catalyst

Perovskite can be synthesized by diverse routes—including sol–gel for single-metal and high-entropy compositions [14], microwave-assisted solvothermal/calcination for hollow architectures [15], co-precipitation/impregnation for composites [16], classical solid-state reaction [17], and template-assisted strategies to tailor porosity and reducibility [18]—while A/B-site substitutions are widely explored in related electro(cata)lytic systems [19–22]. For BaSnO_3 , early studies highlighted the coupling between synthesis parameters and microstructure [23]. Guided by these precedents, and to favor uniform A-site Mg incorporation with controlled particle size/surface area, we adopted a co-precipitation route to prepare BaSnO_3 and $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$, followed by mild H_2 reduction to generate oxygen-deficient phases for CO_2 conversion [24].

Besides, Sergey A. et al. investigated how the shapes and sizes of the metal and oxide parts of the Ni/MeOx catalyst affected its activity and selectivity in the Sabatier reaction [25].

2.1. Preparation of $BaSnO_3$ and $Ba_{0.96}Mg_{0.04}SnO_3$

The sources and purity of all the chemicals used in this work are listed in Table 1.

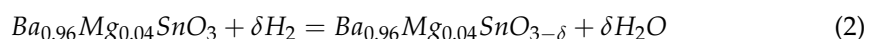
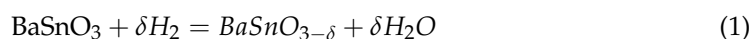
Table 1. The sources and purity of all the chemicals.

Chemical	Purity	Source
$BaCl_2 \cdot 2H_2O$	99.99%	China National Medicines Corporation Ltd.
$SnCl_4 \cdot 5H_2O$	99.99%	China National Medicines Corporation Ltd.
$Mg(NO_3)_2 \cdot 6H_2O$	99.99%	China National Medicines Corporation Ltd.
$C_6H_8O_7 \cdot H_2O$	99.99%	China National Medicines Corporation Ltd.
NaOH solution	4 mol/L	China National Medicines Corporation Ltd.
Deionized water	99.99%	China National Medicines Corporation Ltd.

Stoichiometric $BaCl_2 \cdot 2H_2O$ (234 g) and $SnCl_4 \cdot 5H_2O$ (351 g)—and, for the doped sample, $Mg(NO_3)_2 \cdot 6H_2O$ corresponding to 4% A-site Mg substitution (10 g)—were dissolved separately in deionized water (1 L) to form clear solutions and then combined. Citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) was added as a chelating agent at $1.5 \times$ the total molar amount of metal ions, and the mixture was stirred for 30 min to afford a homogeneous complex. Under magnetic stirring, $4 \text{ mol} \cdot \text{L}^{-1}$ NaOH was added dropwise to adjust $\text{pH} = 12$, promoting co-precipitation; stirring then continued for an additional 2 h. The suspension was allowed to settle, centrifuged, and washed repeatedly with deionized water until the filtrate conductivity was $<10 \text{ } \mu\text{S} \cdot \text{cm}^{-1}$. The precipitate was vacuum-dried at $80 \text{ } ^\circ\text{C}$ for 12 h and calcined in air at $900 \text{ } ^\circ\text{C}$ for 6 h ($5 \text{ } ^\circ\text{C} \cdot \text{min}^{-1}$ heating rate) to obtain the perovskite phase. Tight control of stoichiometry, pH, and thermal treatment favors the uniform incorporation of Mg^{2+} at Ba^{2+} sites and yields high crystallinity.

2.2. Preparation of $BaSnO_{3-\delta}$ and $Ba_{0.96}Mg_{0.04}SnO_{3-\delta}$

Following the optimized window reported in [24], oxygen vacancies were introduced by in-situ H_2 reduction in a temperature-controlled reactor. Specifically, $BaSnO_3$ was reduced at $310 \text{ } ^\circ\text{C}$ and $Ba_{0.96}Mg_{0.04}SnO_3$ at $320 \text{ } ^\circ\text{C}$ under $H_2 = 40 \text{ mL} \cdot \text{min}^{-1}$ for 3 h. Upon completion, the reactor was evacuated for 20 min, purged with Ar for 20 min, and evacuated again for 10 min prior to CO_2 experiments. These conditions reproducibly yielded $BaSnO_{3-\delta}$ and $Ba_{0.96}Mg_{0.04}SnO_{3-\delta}$ suitable for adsorption and cyclic decomposition tests (see Equations (1) and (2) for the stoichiometric representations).



3. Characterization of Catalysts

3.1. Composition Analysis

Inductively coupled plasma analysis (Table 2) shows that the measured compositions closely match the targets: $BaSnO_3$ exhibits Ba:Sn = 0.97:0.99 versus 1:1 (design), and $Ba_{0.96}Mg_{0.04}SnO_3$ exhibits Ba:Sn:Mg = 0.97:0.99:0.041 versus 0.96:1:0.04, with deviations within $\pm 5\%$. These results indicate accurate batching and minimal elemental loss under the chosen synthesis conditions.

Table 2. ICP test results of sample.

Design Values	ICP Test Results
Ba:Sn = 1:1	Ba:Sn = 0.97:0.99
Ba:Sn:Mg = 0.96:1:0.04	Ba:Sn:Mg = 0.97:0.99:0.041

To determine the phase composition of the prepared catalysts, X-ray diffraction (XRD) analysis was performed, and the results were compared with standard reference patterns. As shown in Figure 1, most diffraction peaks of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ match those of BaSnO_3 , while the remaining peaks correspond to MgO . After Mg doping, both the positions and intensities of the diffraction peaks changed noticeably, yet all main peaks could still be indexed to the perovskite phase. The XRD peak shifted to the right, and the most common reason for this shift is lattice defects in the sample. The sharper characteristic peaks of the doped sample indicate improved crystallinity and confirm that Mg was successfully incorporated into the perovskite lattice.

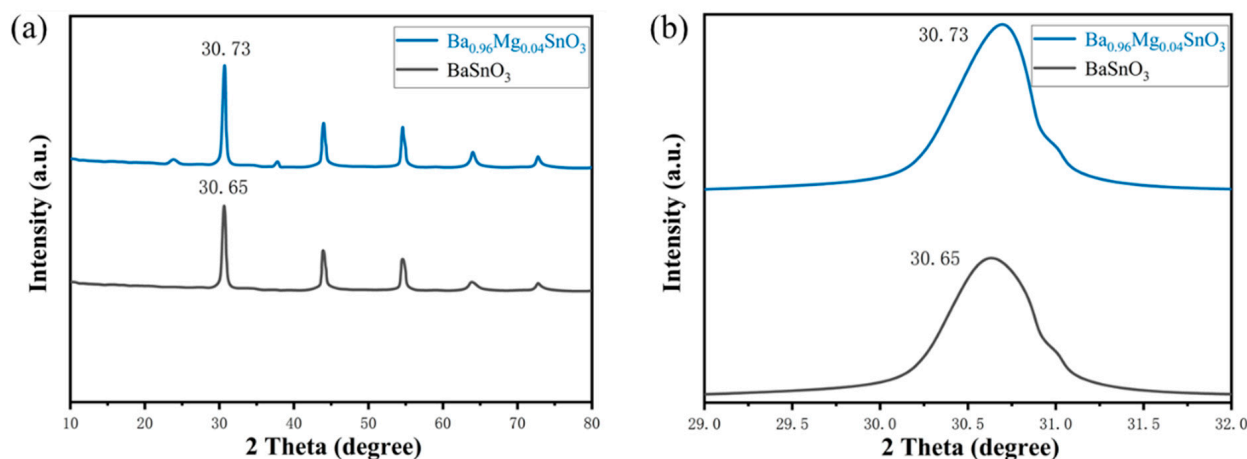


Figure 1. XRD of BaSnO_3 and $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$: (a) full spectra and (b) magnified views.

The strongest diffraction peak of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ appears at $2\theta = 30.73^\circ$, shifted toward a higher angle compared with the strongest peak of BaSnO_3 at $2\theta = 30.65^\circ$. This shift is attributed to the smaller ionic radius of Mg^{2+} relative to Ba^{2+} , whereby partial substitution decreases the interplanar spacing, resulting in a higher 2θ value [26]. The presence of MgO peaks suggests that excessive Mg^{2+} did not disrupt the perovskite lattice but rather formed a separate MgO phase, which may contribute to the enhanced CO_2 selectivity of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$.

3.2. Structural Characterization Analysis

As shown in Figures 2 and 3, by comparing the SEM images of BaSnO_3 and $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$, it was found that the morphology before and after doping was the same, both in the form of particles. However, BaSnO_3 exhibits a relatively rough surface structure, with particles of varying sizes and dense distribution, and agglomeration phenomena in some areas. However, $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ exhibits relatively uniform particle distribution, consistent particle size, and clear gaps between particles, indicating that Mg doping may suppress excessive growth and agglomeration of particles to some extent, making the microstructure of the material more regular.

EDS maps corroborate these observations, the distribution of O, Sn, and Ba elements was relatively wide, presenting a relatively uniform element distribution state overall, which was consistent with the expected composition of BaSnO_3 . In the EDS image of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$, in addition to O, Sn, and Ba elements, Mg element also appeared, and the distribution of Mg element showed a certain point like feature, $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ be demonstrated to have a Mg doped structure from Figure 3. The relatively content of MgO is 0.04%, which indicates that most Mg^{2+} ions are incorporated into the BaSnO_3 lattice rather than forming a separate MgO phase. This minor amount of MgO may slightly influence the catalytic activity of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ but does not change the overall perovskite structure.

This indicated that Mg had been successfully doped into the lattice of BaSnO_3 , but its distribution may not be completely uniform, and it might form enriched regions or exist in the form of a second phase in some areas. This was consistent with the XRD detection finding of MgO characteristic peaks.

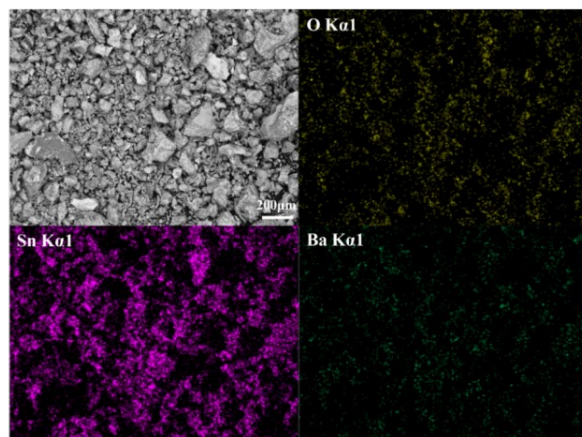


Figure 2. SEM and EDS images of BaSnO_3 .

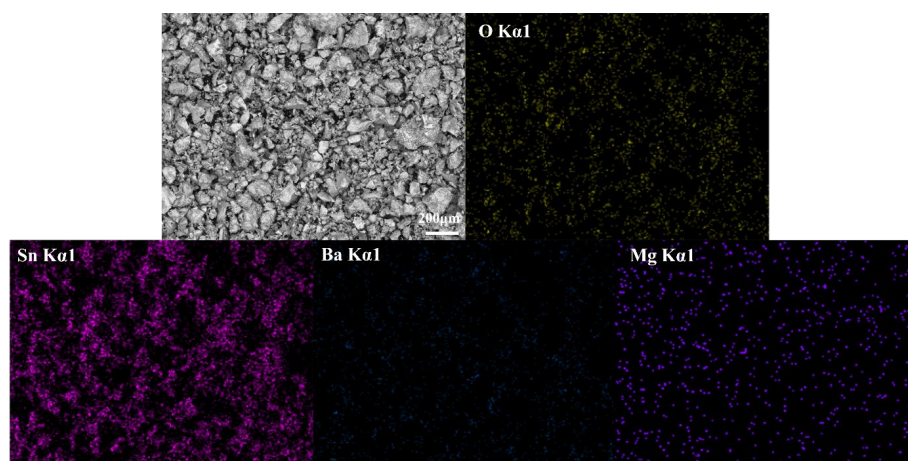


Figure 3. SEM and EDS images of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$.

In this experiment, the particle size was measured using the direct method, the geometric size of the particles was directly observed through electron microscopes, and the “representative size” was obtained.

From Table 3, it can be seen that Mg doping has improved the physical properties of BaSnO_3 , resulting in a reduction in overall particle size and an increase in specific surface area. The average particle size of D50 decreased by 16%, and the specific surface area increased by nearly 26%. It can be inferred that Mg doping can optimize the physicochemical properties of BaSnO_3 and enhance its catalytic performance.

Table 3. Particle size and specific surface area of catalysts in fresh state.

Catalyst	D10 (μm)	D50 (μm)	D90 (μm)	Reduction Rate of Average Particle Size (%)	Specific Surface Area (m ² /g)	Improvement Ratio of Specific Surface Area (%)
BaSnO_3	15.6	38.6	55.2	0	46.4	0
$\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$	13.4	32.4	46.5	16%	58.4	25.7%

4. Discussion

Compared with pure BaSnO_3 , the specific surface area, oxygen storage, thermal stability and structural stability of Mg doped BaSnO_3 have been improved, further inhibiting the sintering agglomeration of BaSnO_3 surface under high temperature environment, and the anti-aging performance of the catalyst has also been improved accordingly. Although BaSnO_3 outperforms in terms of specific surface area and oxygen storage capacity, $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ performs better in catalytic activity testing. Compared to BaSnO_3 , $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ has significantly improved cyclic reaction performance due to its better structural and thermal stability. The lifetime and carbon deposition of cyclic reactions have also been significantly enhanced. Among them, the cyclic reaction times of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ can reach more than 40 times, and the highest carbon deposition can reach 22.54%, whereas the undoped BaSnO_3 catalyst completed only 24 cycles with a maximum carbon deposition rate of 12.68%.

5. Experimental Section

5.1. Oxygen Storage Performance and Anti-Aging Performance Test

5.1.1. Oxygen Storage Performance Test of Catalyst in Fresh State

Oxygen storage performance detection steps are as follows:

Place the sample to be tested in the reactor, introduce H_2 to raise the temperature to $550\text{ }^\circ\text{C}$, and reduce the powder sample product about 3 h, then switch to N_2 blowing, cool the sample to $200\text{ }^\circ\text{C}$, pulse O_2 at constant temperature, and measure the oxygen storage capacity (OSC) according to calculate the sample oxygen storage capacity based on the oxygen adsorption capacity.

The oxygen storage performance test data of the catalysts in fresh state are shown in Table 4.

Table 4. The oxygen storage capacity of the catalysts in fresh state.

Catalyst	Oxygen Storage Capacity ($200\text{ }^\circ\text{C}$) ($\mu\text{mol/g}$)	Change Rate of Oxygen Storage Capacity (%)
BaSnO_3	408	0
$\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$	433	6.1

According to the test data, the measured oxygen storage capacity of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ is $433\text{ }\mu\text{mol/g}$, which is 6.1% higher than that of undoped BaSnO_3 . This proves that Mg doping can enhance the oxygen storage capacity of perovskite BaSnO_3 .

In Mg doping in the presence of impurities, the specific surface area of the catalyst significantly increases, resulting in the contact surface between the catalytic material and the gas reactants correspondingly expands, thereby enhancing its adsorption capacity. Introducing impurity ions into the lattice structure to induce lattice defects by generating and increasing the number of oxygen vacancies, the fluidity of lattice oxygen is improved, significantly enhancing the material's oxygen storage capacity.

5.1.2. Anti-Aging Performance Test

In the anti-aging performance test, a small amount of catalyst powder was selected to be thermally aged at $1200\text{ }^\circ\text{C}$ for 4 h, and then cooled at room temperature after thermal aging. Then the catalyst after thermal aging was analyzed by SEM, and the specific surface area and oxygen storage capacity were measured to analyze its anti-aging performance. The test results are shown in Figures 4 and 5 and Table 5.

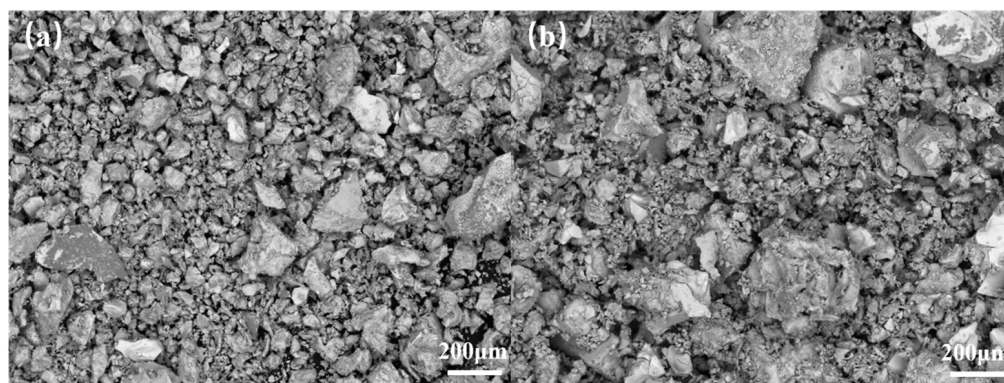


Figure 4. SEM images of BaSnO_3 before and after thermal aging. (a) Before thermal aging of BaSnO_3 ; (b) After thermal aging of BaSnO_3 .

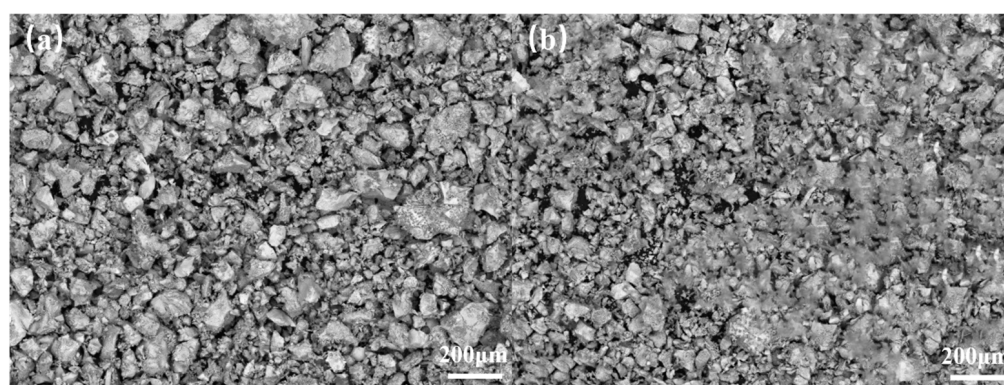


Figure 5. SEM images of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ before and after thermal aging. (a) Before thermal aging of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$; (b) After thermal aging of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$.

Table 5. Specific surface area and oxygen storage capacity of catalyst after thermal aging.

Catalyst	Specific Surface Area (m^2/g)	Reduction Rate of Specific Surface Area (%)	Oxygen Storage Capacity (200°C) ($\mu\text{mol}/\text{g}$)	Reduction Rate of Oxygen Storage Capacity (%)
BaSnO_3	19.7	57.7	256	37.3
$\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$	28.7	50.8	341	21.2

(1) SEM analysis of catalyst after thermal aging

By comparing Figure 4a,b, it was found that after thermal aging treatment, the particles underwent sintering and the particle size significantly increased, with a small number of small particles. However, by comparing Figure 5a,b, it could be seen that although sintering occurred in the aged particles, there was no obvious agglomeration phenomenon, and the particle size was basically the same as before aging. This may be because Mg doping enhanced the dispersion of other components, thus avoiding the agglomeration between grains, that is, Mg doping improved the anti-aging performance of perovskite BaSnO_3 .

(2) Specific surface area and oxygen storage capacity of catalyst after thermal aging

From the data in Table 5, it could be seen that after the 1200°C thermal aging experiment, the specific surface area and oxygen storage capacity of the sample decreased due to the sintering phenomenon at high temperatures. In the absence of doping, the specific surface area decreased from $46.42 \text{ m}^2/\text{g}$ to $19.65 \text{ m}^2/\text{g}$, with a reduction rate of 57.7%. In the case of Mg doping, the specific surface area decreased from $58.35 \text{ m}^2/\text{g}$ to $28.71 \text{ m}^2/\text{g}$,

with a reduction rate of 50.8%; At the same time, the reduction rate of oxygen storage under doping was significantly lower than that without doping, and the reduction rate of Mg doping was only 21.2%, which was much lower than that of undoped 37.3%. Therefore, Mg doping can enhance the thermal aging resistance of BaSnO_3 .

5.2. Adsorption Performance and Catalytic Activity Testing

5.2.1. Gas Adsorption Performance Test

In multiphase catalytic reactions, the adsorption and activation of gaseous reactants on the surface of catalyst powder is a prerequisite for the start of the catalytic reaction, forming an activated adsorption state, reducing the activation energy of the reaction process, and thus promoting the progress of the reaction.

After pretreatment of the catalyst powder, a programmed temperature fixed reactor was used as the adsorption test platform to determine its adsorption performance for CO_2 . The specific operation was as follows: 20 g of ground catalyst was weighed, evenly spread on a stainless-steel plate, and placed in a temperature-controlled reactor. Firstly, Argon (Ar) was blown into the chamber at 400 °C for 1 h to remove the gas and moisture adsorbed on the surface of the catalyst powder. Subsequently, the temperature was lowered to 200 °C in an Ar atmosphere, then CO_2 was blown into the chamber. When CO_2 concentration was 1000 ppm (with Ar as the equilibrium gas), the temperature was programmed to 500 °C, at the same time CO_2 concentration values was measured every minute.

Figure 6 shows the CO_2 concentration change curve of the catalyst before and after Mg doping in the CO_2 adsorption experiment. The simulated gas composition is a mixture of CO_2 +Ar, with a CO_2 concentration of 1000 ppm. When the concentration of CO_2 decreases, it indicates the adsorption capacity of CO_2 on the catalyst surface.

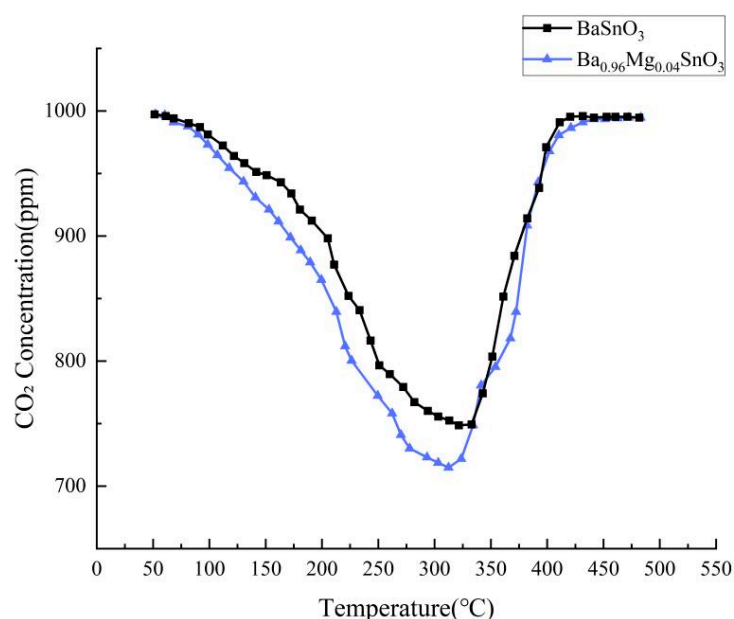


Figure 6. CO_2 adsorption curves before and after Mg doping.

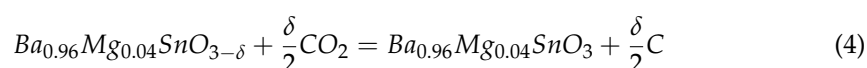
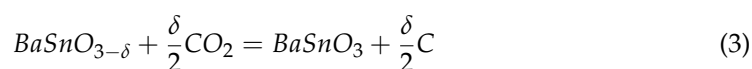
From Figure 6, it can be seen that there are two obvious concave regions in the concentration change curve. The adsorption curve of $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ has a higher degree of concave at around 130 °C compared to BaSnO_3 . The main reason for this is that the doped catalyst has an increased specific surface area, improved contact state, and thus better physical adsorption performance.

As the temperature increases, the catalyst is mainly activated through chemical adsorption. The CO_2 adsorption rate accelerates and the adsorption amount increases accordingly.

The intermolecular forces drive the CO₂ gas to adsorb in the oxygen vacancy of the catalyst. Compared with the adsorption curve of BaSnO₃, the slope of the adsorption curve of Ba_{0.96}Mg_{0.04}SnO₃ is larger at around 200 °C, and it shows a significant downward shift, and indicates a faster CO₂ adsorption rate and a higher CO₂ adsorption capacity at the same temperature. The adsorption peak shifts significantly downwards, and the CO₂ adsorption rate at the highest peak is about 28.3%. At all high temperature stages, its decreasing slope and adsorption amount are greater than those of BaSnO₃, it indicates that Mg doping improves the CO₂ adsorption rate and adsorption amount of BaSnO₃.

5.2.2. Catalytic Activity Testing

A temperature-controlled reactor was employed as the catalytic reaction platform to evaluate catalyst activity. 20 g of catalyst were loaded into the reactor, and oxygen-deficient catalysts (BaSnO_{3-δ}, Ba_{0.96}Mg_{0.04}SnO_{3-δ}) were generated in situ under a hydrogen atmosphere at a reduction temperature of 320 °C, with a hydrogen flow rate of 40 m·min⁻¹ for 3 h. Upon completion of the reduction, the reactor was evacuated for 20 min using a vacuum pump, purged with argon for 20 min, and evacuated again for 10 min. CO₂ was then introduced into the reactor for the catalytic activity test until the pressure reached 0.1 MPa, and the pressure-time (P-t) data were recorded immediately. The total reaction time for each cycle was 2–4 h. When the number of reaction cycles reached a certain threshold, complete CO₂ reduction could no longer be achieved. Before initiating the next cycle, the residual gas in the reactor was evacuated, and hydrogen was reintroduced to regenerate the catalyst. After all cyclic reactions were completed, the samples were cooled to room temperature, and carbon deposition was quantified using an elemental analyzer. The reaction equations involved in the process were as follows:



As shown in Figure 7, the CO₂ pressure drop in the first two reaction cycles of BaSnO₃ was close to 1. With increasing cycle number, the pressure drop decreased in a stepwise manner. By the 11th cycle, BaSnO₃ maintained a decomposition rate above 60%. From the 13th to the 16th cycle, the CO₂ conversion rate plateaued at approximately 50%. Between the 18th and 20th cycles, the conversion rate stabilized at around 33%, indicating that the catalyst still retained some CO₂ reduction capability. At the 21st cycle, the conversion rate sharply declined to 20%, and by the 24th cycle, it dropped to about 10%, rendering CO₂ decomposition nearly impossible.

For Ba_{0.96}Mg_{0.04}SnO₃, the CO₂ pressure drop also decreased progressively with increasing cycle number; however, the decline in conversion rate was markedly slower than that of BaSnO₃, indicating superior retention of catalytic activity. As summarized in Table 6, 4% Mg doping substantially enhanced the cyclic reaction performance, operational lifetime, and carbon deposition capacity. The Ba_{0.96}Mg_{0.04}SnO₃ catalyst achieved up to 40 reaction cycles with a peak carbon deposition rate of 22.54%, whereas the undoped BaSnO₃ catalyst completed only 24 cycles with a maximum carbon deposition rate of 12.68%.

Table 6. The number of cyclic reactions and carbon deposition of catalysts.

Catalyst (20 g)	Number of Cyclic Reactions	Carbon Deposition (g/%)
BaSnO ₃	24	2.54/12.68%
Ba _{0.96} Mg _{0.04} SnO ₃	40	4.51/22.54%

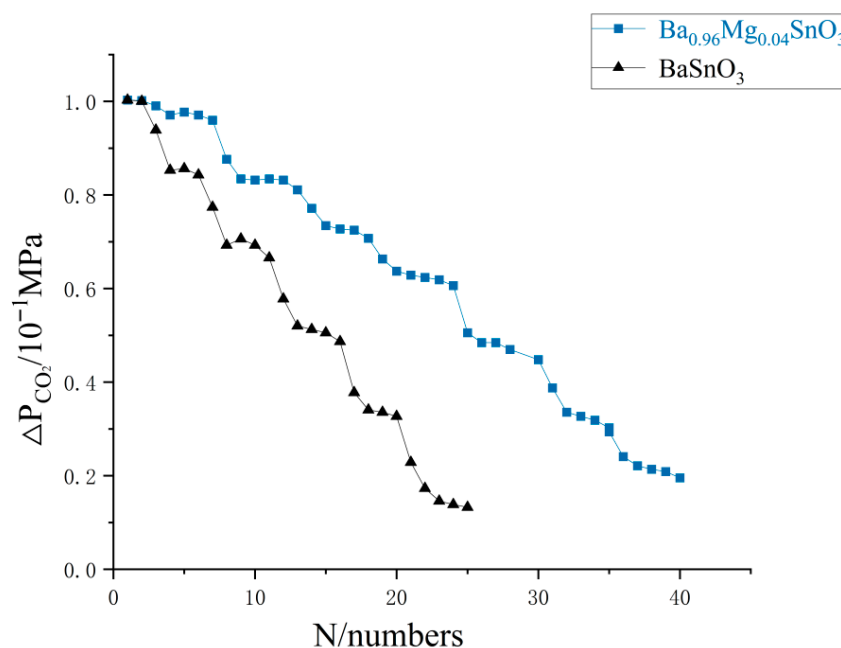


Figure 7. CO₂ pressure drops variation curve with the number of cycles.

From the data in Table 5, it could be seen that after 4% Mg doping, the cyclic reaction performance, lifetime, and carbon deposition of BaSnO₃ have been greatly improved and enhanced. The maximum number of cyclic reactions for Ba_{0.96}Mg_{0.04}SnO₃ was 40, with a maximum carbon deposition rate of 22.54%, while the maximum number of cyclic reactions for BaSnO₃ was 24, with a maximum carbon deposition rate of 12.68%. Although doping makes the structure more stable, with the increase of doping amount, the degree of oxygen vacancy δ is positively correlated with CO₂ decomposition activity [27], making it easier for CO₂ to adsorb on its surface.

Figure 8a,b presents the XRD patterns of BaSnO₃ and Ba_{0.96}Mg_{0.04}SnO₃ after different numbers of reaction cycles. With increasing cycle number, the characteristic diffraction peaks of both catalysts gradually weakened, accompanied by the emergence of strong SnO₂ peaks and weak BaO peaks. This indicates a progressive reduction in the proportion of the perovskite phase, with increasing SnO₂ content and decreasing BaO content, until BaSnO₃ was completely decomposed in the system. Notably, under the same number of cycles, Ba_{0.96}Mg_{0.04}SnO₃ retained stronger perovskite peaks than BaSnO₃, confirming that Mg doping enhances structural stability. The doped catalyst's oxygen-deficient lattice was less prone to collapse, thereby slowing the disintegration of the crystal structure, extending the cyclic reaction lifetime, and promoting higher carbon deposition.

As shown in Figure 9, it has been experimentally proven that the activity of catalyst Ba_{0.96}Mg_{0.04}SnO₃ gradually increases with the increase of Mg doping ratio starting from 1%, and reaches its highest point at 4%. Subsequently, as the Mg doping ratio increased, the activity of the catalyst actually decreased, which was attributed to the decrease in Ba element content leading to a decrease in catalyst activity.

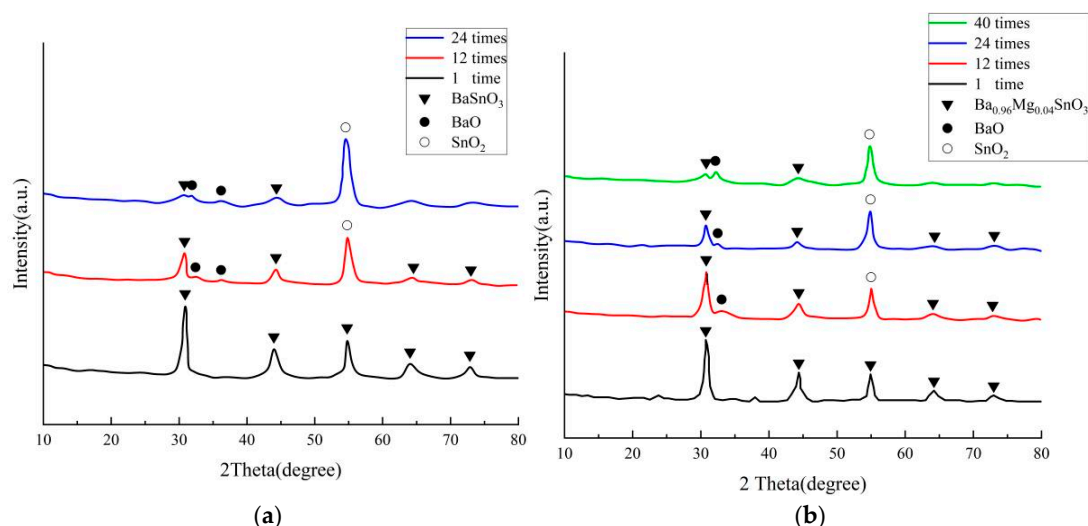


Figure 8. XRD diffraction patterns of (a) BaSnO_3 , (b) $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ under different cycle reaction times.

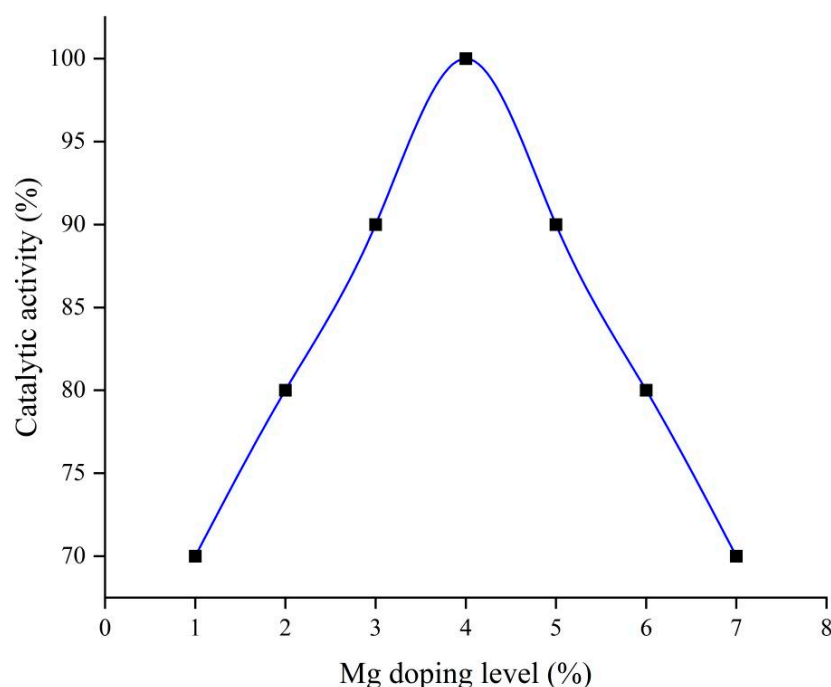


Figure 9. Catalytic activity change with the doping level of Mg.

6. Conclusions

The research objective of this paper is to reduce CO_2 emissions from marine diesel engines. It innovatively proposes the use of perovskite catalysts to decompose CO_2 from diesel engine. The research methods used are to modify BaSnO_3 catalyst by partially replacing Ba with 4% Mg doped BaSnO_3 . The physicochemical properties of BaSnO_3 and $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ catalyst were characterized using ICP, OSC, SEM, and EDS techniques, while their CO_2 adsorption and catalytic performance were systematically evaluated.

The results show that Mg doping effectively enhances the specific surface area, oxygen storage capacity, structural stability, and thermal stability of BaSnO_3 . These improvements suppress surface sintering and agglomeration at high temperature and significantly strengthen the catalyst's anti-aging capability. Consequently, $\text{Ba}_{0.96}\text{Mg}_{0.04}\text{SnO}_3$ exhibits higher catalytic activity and better cyclic stability than undoped BaSnO_3 . Its cyclic reaction

lifetime and carbon deposition performance are also improved, with stable operation for more than 40 cycles and a maximum carbon deposition ratio of 22.54%.

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