Sn promoted BaFeO_{3-δ} catalysts for N₂O decomposition: Optimization of Fe active centers

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Abstract

A series of $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ catalysts were prepared by sol-gel method and tested for N_2O decomposition to shed light on the effect of B-site substitution on the catalytic behavior of perovskite catalysts. ^{119}Sn and ^{57}Fe Mössbauer results confirmed that the 5-fold coordinated Fe^{3+} cations with one adjacent oxygen vacancy ($\text{Fe}^{3+}\text{-O}_5$) were the main active centers for N_2O decomposition. Doping of Sn cations can significantly improve the percentage of $\text{Fe}^{3+}\text{-O}_5$ from 30% ($x = 0$) to 68% ($x = 0.8$). More importantly, the valence state of Fe could be gradually reduced due to weakening of Fe-O bond with increasing the Sn content, which was attributed to the stronger force of Sn than Fe in Fe-O-Sn structure to draw the oxygen anion and expansion of unit cell volume. Such change of Fe chemical state favored the oxygen mobility of the catalyst, leading to reduction of activation energy for N_2O decomposition from ca. 241 ($x = 0$) to 178 kJ mol^{-1} ($x = 0.8$). $\text{BaFe}_{0.2}\text{Sn}_{0.8}\text{O}_{3-\delta}$ catalyst exhibited the highest intrinsic rate of 1.49 s^{-1} (550 °C), nearly 4 times larger than $\text{BaFeO}_{3-\delta}$ (0.43 s^{-1}).

Keywords: perovskite; B-site substitution; oxygen mobility; Mössbauer spectroscopy; N_2O decomposition

1. Introduction

Catalytic decomposition of high concentration nitrous oxide (N_2O) has been a topic of interest for decades, since it was crucial for ignition of N_2O propellant for small satellite or abatement of N_2O from adipic acid industry for emission control ^[1-4]. Decomposition of N_2O into N_2 and O_2 is a strongly exothermic process ($\Delta_r H^\circ \approx -82$ kJ/mol) with maximum temperature in the propulsion system or reactor exceeding 1000 °C ^[5-7]. Therefore, the qualified catalysts should combine the features of both high activity and thermal stability.

Iron based materials are among the most active catalysts for N_2O decomposition ^[8-11]. Considerable researches on decomposition of diluted N_2O (ppm level) revealed that the activity of these catalysts was closely related to the structure and local environment of iron species ^[12-14], and many researchers attempted to understand this particular feature in their work, which is of crucial importance for synthesis of Fe containing materials with optimized catalytic properties. Pirngruber et al.^[15] demonstrated that the activity of different Fe species in Fe-ZSM-5 catalyst followed the order of monomeric Fe^{3+} , dimeric $\text{Fe}^{3+} >$ oligomeric Fe species $>$ Fe_2O_3 particles. After high temperature treatment, the oligonuclear and cationic Fe species can be converted to Al stabilized Fe-O-Al species, resulting in increased reaction rate for N_2O decomposition ^[16]. Sazama et al.^[17] found that increasing the framework Al atoms in Fe-ZSM-5 greatly enhanced the catalytic activity of cationic Fe species. As for iron oxides, studies by Li et al.^[18] and Pinaeva et al.^[19] suggested that their redox properties can be improved by doping of Al or loading them on suitable carriers, which resulted in improved catalytic activity towards N_2O decomposition.

Perovskite oxides are an important class of functional materials that have been widely studied for the high temperature reactions, e.g. N_2O and NO decomposition ^[20, 21]. These catalysts have the

general formula ABO_3 , where A stands for the lanthanide, alkaline, or alkaline-earth cations, and B mainly represents the transition metal cations, which normally act as the active centers ^[22]. Partial replacement of B by foreign cations can greatly adjust the nature (valence state and coordination condition) of B cations, enabling the perovskite oxides to exhibit a broad diversity of properties ^[23, 24]. However, the electronic properties of the transition metals were so complex that effect of B-site doping was hard to be fully understood. For example, Iwakuni et al.^[25] studied the NO decomposition on $BaMn_{1-x}B'_xO_3$ catalysts, and found that the activity increased in the order of $Mg > Zr > Fe > Ni > Sn > Ta$, for which no apparent correlation was observed between the catalytic performance and the valence state or ionic radius of B' cations at all. The Fe cations can exist in various valence states (Fe^{3+} and Fe^{4+}) and coordination conditions (4-, 5- and 6-fold coordination with oxygen) in the perovskite matrix ^[26, 27], feature of which determined the activity of these catalysts. Shin et al.^[28] investigated the NO decomposition on $SrFeO_{3-\delta}$, and proposed that the most active centers should be assigned to the trivalent Fe cations with four adjacent lattice oxygen and two oxygen vacancies ($Fe^{3+}-O_4$). The state of Fe ions in perovskite oxides can be altered by B-site substitution. As indicated by Ciambelli et al.^[29], the activity of Fe cations in $LaFe_{1-x}Al_xO_3$ catalysts towards CO oxidation was greatly increased with the Al content, since Al doping improved the oxygen mobility of the catalyst. As for N_2O decomposition, a number of studies on Fe-based perovskite catalysts have been done these years, however, few reports focused on investigation of the structure of Fe active centers ^[30-32]. Only Kartha et al. ^[33] have pointed out that the enhanced performance of Ti modified $LaFeO_3$ catalysts was closely related to the generation of oxygen vacancies and asymmetric environment around Fe cations. To date, the knowledge about the correlation between the nature of Fe cations in perovskite oxides, including electronic structure and

coordination conditions, and the N₂O decomposition activities was far from enough.

The Sn cations, which have been used as promoter for NO reduction and CO oxidation reactions [34, 35], can be well mixed with Fe ions in perovskite matrix [36, 37]. In this work, we selected BaFe_{1-x}Sn_xO_{3-δ} as a model catalyst, and the effect of Sn doping on electronic structure and coordination of Fe cations in BaFe_{1-x}Sn_xO_{3-δ} was thoroughly investigated by sensitive ⁵⁷Fe and ¹¹⁹Sn Mössbauer spectroscopy on the atomic scale [38, 39]. The influence of these changes on the catalytic performance for high concentration N₂O decomposition was studied and the active sites for N₂O decomposition were determined. On this basis, a clear picture on the correlation between structure of Fe active centers and the corresponding catalytic behavior was proposed.

2. Experimental

2.1. Catalyst preparation

The BaFe_{1-x}Sn_xO_{3-δ} (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) catalysts were prepared using sol-gel method as reported [40]. Ba(CH₃COO)₂ (AR, Kermel, Tianjin, China), SnC₂O₄ (CP, Aladdin, Shanghai, China), Fe(NO₃)·9H₂O (99.99%, Aladdin, Shanghai, China), citric acid (AR, Kermel, Tianjin, China), H₂O₂ aqueous solution (30%, Kermel, Tianjin, China), and ammonia solution (25%, Kermel, Tianjin, China) were used as raw materials for the preparation.

In a typical procedure, specific amount (depends on the specific catalyst; e.g. 4.135 g for x = 1.0 sample) of SnC₂O₄ was dissolved in 50 ml mixture of deionized (DI) water and H₂O₂ aqueous solution (volume ratio of DI water to H₂O₂ solution equals to 5) at 80 °C, and the obtained solution was cooled to room temperature. Subsequently, citric acid (Sn/citric acid molar ratio = 1/6) was introduced to the solution, and the pH was adjusted to around 7 by dropwise adding of ammonia solution. The Ba/Fe mother solution was prepared by dissolving stoichiometric Fe(NO₃)·9H₂O and

Ba(CH₃COO)₂ in 100 ml DI water. Then citric acid (total metal ions/citric acid molar ratio = 1/6) was added to the solution and pH was also adjusted to around 7 with ammonia solution.

The above two solutions were mixed at room temperature, and concentrated to viscous gel at 80 °C afterwards. The gel was dried at 150 °C overnight, and then preheated to 450 °C for 4 h in air to remove organic species. After an intermediate grinding, the powders were further calcined at 1200 °C for 4 h in air to obtain the final BaFe_{1-x}Sn_xO_{3-δ} catalyst.

2.2. Catalyst characterization

The phase composition were analyzed by XRD on a PANalytical X'Pert-Pro powder X-ray diffractometer (U=40 kV, I=40 mA) using Cu K_α radiation in the angle interval from 20 to 80° (2θ), with a step size of 0.0334° (2θ) and a counting time of 19.685s for one step. The lattice parameters of the obtained catalysts were calculated based on all diffraction peaks. Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen adsorption at -196 °C using a Quadrasorb SI instrument. The ¹¹⁹Sn Mössbauer spectra were collected at room temperature using ¹¹⁹Sn in the BaSnO₃ as an emitter, and the isomer shift (IS) was given with respect to the centroid of BaSnO₃ at room temperature. ⁵⁷Fe Mössbauer spectra were collected at room temperature using ⁵⁷Co γ-quantum source in the Rh matrix and the IS value was set with respect to that of α-Fe at room temperature. All spectra were computer-fitted by Lorentzian curves with a least-squares fitting procedure. XPS experiment was performed on an ESCALAB 250Xi instrument to determine the surface composition and the binding energies of the catalysts. The binding energy was calibrated using the adventitious carbon (C1s peak at 284.6 eV). The morphologies were investigated by a field-emission scanning electron microscopy (SEM, JEOL JSM-7800F).

According to the BET result, the average particle size (D, m) was estimated with the assumption

of a sphere model by the fomula: $D = 6 / (1000 * S * \rho)$, where S and ρ represent the specific surface area (m^2/g) and density (kg/m^3), respectively. The density for $\text{BaFeO}_{3-\delta}$ and BaSnO_3 is determined to be $5900 \text{ kg}/\text{m}^3$ and $7240 \text{ kg}/\text{m}^3$, respectively.^[41, 42] Due to the unavailable data for $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0.2 \leq x \leq 0.8$), the density of these samples is roughly calculated by the formula: $\rho_x = 7240x + 5900(1-x)$.

O_2 -TPD was carried out on the Micromeritics Autochem 2920 apparatus to monitor the reducibility of the perovskite. For a typical O_2 -TPD measurement, 0.15 g catalyst was loaded in a U-shape quartz tube. Then pure helium (30 ml/min) was introduced to the tube as carrier gas and the temperature was programmatically raised to 900°C at a ramp rate of $10^\circ\text{C}/\text{min}$. The effluent gases were analyzed with a quadrupole mass spectrometer (OMNISRRAR, GSD-300). The amount of O_2 released in this process was calibrated by using a calibration gas with known concentration.

2.3. Activity test

The kinetic data for N_2O decomposition was collected on a fixed-bed quartz reactor (i.d. = 8 mm) as described in the literatures^[43-45]. In a typical experiment, the catalyst was carefully grinded in a mortar to ensure no internal mass transfer limitation. Then, a certain amount of the catalyst powders (20 ~ 50 mg) with grain size of below $75 \mu\text{m}$ was diluted with 150 mg quartz powders (inert for N_2O decomposition at the applied reaction temperature) and packed in the reactor. A 3 ~ 5 mm quartz bed was placed above the catalyst bed to ensure uniformity of the inlet mixture gas. Another 3 ~ 5 mm quartz bed was located downstream to hold the catalyst bed and avoid backmixing of the gas. The gases (N_2O , N_2 , O_2 and Ar) were fed to the reactor with four mass flow controllers, and a total flow of 110 ml/min (which was determined based on the experiment to exclude the external mass transfer limitations) was used for all the experiments. The contact time was almost the same for all catalysts

and equal to ca. 100 ms. Two thermocouples were placed just above and below the catalyst bed to ensure that no notable temperature gradient existed.

The N₂O decomposition (30 vol%, Ar balance) apparent activation energy (E_a) was determined by varying the temperature over a range of 80 °C (530 ~ 590 °C for $x = 0.6$ and 0.8 samples, 550 ~ 610 °C for $x = 0, 0.2$ and 0.4 samples, and 590 ~ 650 °C for $x = 1.0$ samples, respectively) while the total flow was kept constant (110 ml/min) to ensure no external mass transfer limitations. The reaction order with respect to O₂ was measured by varying the concentration of O₂ (5 ~ 20%). Considering that decomposition of N₂O would generate O₂, the N₂O concentration in such experiment was reduced to 10%, which can reduce the deviation for oxygen concentration. Different reaction temperatures were applied in the experiment to maintain the conversion of N₂O below 10%. The reaction was held for 0.5 h before the analysis to ensure that steady state is reached. The composition of effluent gas was analyzed using an Agilent 6890N gas chromatograph equipped with Molecular sieve 13X and Porapak Q columns and a thermal conductivity detector. It was noteworthy that the amount of Fe centers used for TOF calculation was determined based on the XPS (surface atomic concentration) and BET surface area data ^[31, 46], since the surface feature of the catalysts were close to that in the body and no available information for the exact number of active centers was obtained from chemisorption measurements. The intrinsic activity is calculated using the formula: TOF = converted N₂O molecules per second / surface Fe atoms. The result may be rough, but the magnitude of the TOF data should be right and useful. The conversion (x) of N₂O is determined by comparing the concentration of N₂O in the outlet stream with the initial inlet concentration. The reaction rate is calculated using the formula: $r = C \cdot F \cdot x / V_m$, where F is the total flow through the reactor, V_m is the molar volume of feeding gas and C is the concentration of N₂O (30% or 10%).

Catalytic performance of $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ samples for N_2O decomposition was also investigated by temperature-programmed (400 ~ 800 °C) steady state experiments. In a typical N_2O decomposition experiment, 200 mg catalyst was packed in the reactor. The reactant stream contains 30 vol% N_2O in Ar with the total flow rate of 110 ml/min (STP), corresponding to a gas hour space velocity (GHSV) of 30000 h^{-1} .

To confirm the active centers for N_2O decomposition, $\text{BaFe}_{0.8}\text{Sn}_{0.2}\text{O}_{3-\delta}$ catalyst was selected as a case study. Firstly, $\text{BaFe}_{0.8}\text{Sn}_{0.2}\text{O}_{3-\delta}$ was pretreated in inert Ar to liberate partial lattice oxygen following the same procedure in O_2 -TPD experiment, and then the catalyst was reused for N_2O (30 vol%) decomposition, where the reaction was performed at 550 °C for 0.5 h and cooled to room temperature in the N_2O (30 vol%) atmosphere. After that, the ^{57}Fe Mössbauer spectroscopy measurement was performed to investigate the chemical state of Fe species after the reaction.

3. Results

3.1. Catalytic performance for N_2O decomposition

Fig.1. (a) Arrhenius plot of $\ln r$ versus $1/T$ for N_2O (30 vol% N_2O in Ar) decomposition over $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 1.0$) catalysts and (b) evolution of the specific and intrinsic rate with the Sn content x at 550 °C. Note: ^a surface rate was normalized by surface area of catalyst; ^b The number of Fe centers at catalyst surface was estimated from XPS and BET surface area data.

Fig. 1a displayed the Arrhenius plots of N₂O (30 vol% N₂O in Ar) decomposition over the BaFe_{1-x}Sn_xO_{3-δ} catalysts (0 ≤ x ≤ 1.0). One can notice that each line showed reasonable linearity in the temperature range explored in this study. The apparent activation energies (E_a) of N₂O decomposition were estimated from the slope of the Arrhenius plots. The calculated E_a values were in the range of 178 ~ 248 kJ mol⁻¹, which matched well with previous reports for Fe based catalysts (150 ~ 240 kJ mol⁻¹ for LaFeO₃, EuFeO₃, and Fe-ZSM-5 etc.)^[31, 32, 47]. For pure BaSnO₃ (x = 1) catalyst, it exhibited the lowest surface rate of all the catalysts. In contrast, the reaction rate over pure BaFeO_{3-δ} (x = 0) catalyst was significantly increased, which demonstrated that Fe cations were far more active than Sn and accounted for the main active centers for N₂O decomposition. It was interesting to notice that reaction rate of BaFe_{1-x}Sn_xO_{3-δ} catalysts (0.2 ≤ x ≤ 0.8) with both Fe and Sn cations was higher than that of pure BaFeO_{3-δ} (x = 0) and BaSnO₃ (x = 1), which was also confirmed by a typical steady state experiment (Fig. S1). Such result indicated that doping of Sn could effectively enhance the catalytic performance of Fe cations towards N₂O decomposition.

The surface rate at 550 °C was compared to evaluate the effect of Sn content on the catalytic behavior of the BaFe_{1-x}Sn_xO_{3-δ} catalysts (0 ≤ x ≤ 0.8) and the results were shown in Fig. 1b. For undoped BaFeO₃ sample (x = 0), the rate was calculated to be 11.0 mmol_{N₂O} m⁻² h⁻¹, which was comparable to that of BaCoO₃ catalyst (ca. 14.4 mol_{N₂O} m⁻² h⁻¹) and much better than LaCoO₃ (ca. 0.43 mmol_{N₂O} m⁻² h⁻¹)^[48]. For doped samples, the surface rate was similar for all the catalysts, although the content of Fe active cations was actually notable reduced with increasing the Sn content. Such result gave a clue that the activity of Fe cation towards N₂O decomposition was improved with the Sn content, since the concentration or the amount of Fe at the surface (per square meter) was diluted for the samples with higher Sn. To estimate the intrinsic activity of Fe species, the TOF values

were calculated and showed in Fig. 1b. One can see that the TOF of $\text{BaSn}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (1.49 s^{-1}) is nearly 4 times larger than that of undoped $\text{BaFeO}_{3-\delta}$ catalyst (0.43 s^{-1}), suggesting that introduction of Sn cations into $\text{BaFeO}_{3-\delta}$ significantly enhanced the performance of Fe active centers. This was also supported by the evolution of E_a values (Fig. 1a). The E_a of Fe-containing $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ catalysts ($0 \leq x \leq 0.8$) gradually decreased with increasing the x value and a lowest E_a of $178 (\pm 3) \text{ kJ mol}^{-1}$ was reached for the $x = 0.8$ sample. The above results demonstrated that introduction of Sn cations into $\text{BaFeO}_{3-\delta}$ optimized the active centers for N_2O decomposition, which resulted in lowered activation barrier.

3.2. Basic characterization

3.2.1. XRD and BET

Fig. 2 displayed the XRD patterns of the as-prepared $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 1.0$) samples. All samples showed single perovskite phase and no impurities such as BaCO_3 , SnO_2 and Fe_2O_3 were detected (Fig. 2a). For $x = 0$ sample, the diffraction peaks were close to that of $\text{BaFeO}_{2.67}$ [JCPDS 20-0129] with rhombohedral structure. On the incorporation of minor Sn ($x = 0.2$), surprisingly, a cubic perovskite structure were formed. Further increase of Sn loading until to $x = 1.0$, the cubic structure was still maintained, implying that doping of Sn in $\text{BaFeO}_{3-\delta}$ induced the formation of cubic perovskite structure.

Fig. 2. (a) X-ray diffraction patterns of $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 1.0$) samples, and (b) magnified XRD patterns of $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0.2 \leq x \leq 1.0$) in the range of $30.0 \sim 32.0^\circ$ (2θ).

To be noted, the increase of Sn content resulted in a continuous shift of the reflection peaks of $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0.2 \leq x \leq 1.0$) with cubic structure towards lower 2θ values, which was illustrated better in the magnified XRD patterns (Fig. 2b). This result suggested that the cell volume expanded with the Sn content due to the larger radius of Sn^{4+} ($\text{Sn}^{4+} = 0.69 \text{ \AA}$) than the Fe cations ($\text{Fe}^{3+} = 0.645 \text{ \AA}$, $\text{Fe}^{4+} = 0.58 \text{ \AA}$). The lattice parameters (a_0) of $x = 0.2 \sim 1.0$ samples were calculated based on the XRD results and given in Table 1. For $x = 0.2$ sample, the cell constant was $4.073 \text{ \AA}$, a little larger than that of cubic BaFeO_3 ($a_0 = 3.971 \text{ \AA}$, Fe-O bond length $1.986 \text{ \AA}$)^[49]. With increasing the Sn content, the a_0 value was gradually raised from $4.088 \text{ \AA}$ ($x = 0.4$) to $4.116 \text{ \AA}$ ($x = 1$), accompanied with the elongation of B-O (Sn/Fe-O) bond from $2.036 \text{ \AA}$ for $x = 0.2$ to $2.058 \text{ \AA}$ for $x = 1.0$ (Table 1). Besides, one can notice that the variation of estimated Fe-O bond from $x = 0.2$ to 1.0 ($0.022 \text{ \AA}$) was much smaller than the ionic radius difference between Fe^{3+} and Sn^{4+} . Such result gave a clue that the concentration of oxygen vacancies may reduced after introduction of Sn cations, since generation of oxygen vacancies in perovskite oxides normally led to lattice expansion.^[50]

The BET specific areas determined by nitrogen adsorption were also listed in Table 1. Pure $\text{BaFeO}_{3-\delta}$ ($x = 0$) showed a low surface areas of $0.9 \text{ m}^2/\text{g}$, while the Sn containing samples ($x = 0.2 \sim$

1.0) presented higher surface areas ($1.8 \sim 5.9 \text{ m}^2/\text{g}$). In particular, the $\text{BaFe}_{0.2}\text{Sn}_{0.8}\text{O}_{3-\delta}$ sample with highest Sn/Fe ratio exhibited the highest value of $5.9 \text{ m}^2/\text{g}$. This could be further visualized from the SEM images in Fig. S2. The pure $\text{BaFeO}_{3-\delta}$ sample (Fig. S2a) was mainly composed of nonporous monoliths with the size ranging from 1 to 20 μm . Once the Sn ($x = 0.2$) was introduced into the perovskite, the size of the particles was reduced to below 5 μm (Fig. S2b). As the Sn content increased to $x = 0.4 \sim 1.0$ (Fig. S2c $\sim$ 2f), the grain size of the catalysts was further decreased, and a minimized size of ca. 200 nm was obtained for $x = 0.8$ sample. The average particle size was calculated according to the BET results. As shown in Table 1, the size of $x = 0$ sample was ca. 1.13 μm while that of $x = 0.8$ sample was only 0.15 μm . The above results suggested that the introduction of Sn ions into the $\text{BaFeO}_{3-\delta}$ structure could improve the heat resistance of the material to some content.

Table 1. Chemical and physical parameters for $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 1.0$) catalysts.

Samples	Structure / a_0 , ^a Å	B-O bond length, ^b Å	SSA, m^2/g	Particle size, ^c μm
$x = 0$	Rhombohedral / -	-	0.9	1.13
$x = 0.2$	Cubic / 4.073	2.036	1.8	0.54
$x = 0.4$	Cubic / 4.088	2.044	2.2	0.42
$x = 0.6$	Cubic / 4.104	2.052	4.8	0.19
$x = 0.8$	Cubic / 4.110	2.055	5.9	0.15
$x = 1.0$	Cubic / 4.116	2.058	3.4	0.24

^a Relative accuracy $\pm 0.001 \text{ Å}$.

^b Average B-O bond length in cubic structure was supposed to be half of the cell parameter.

^c The particle size was estimated according to the BET result.

3.2.2. O_2 -TPD

Fig. 3. O₂-TPD profiles of the BaFe_{1-x}Sn_xO_{3-δ} (0 ≤ x ≤ 1.0) catalysts and the amount of released O₂.

It is generally accepted that the oxygen mobility of catalysts plays a crucial role in N₂O decomposition reaction, in which the desorption of oxygen is regarded as the rate-limiting step^[51]. O₂-TPD experiments were conducted for BaFe_{1-x}Sn_xO_{3-δ} (0 ≤ x ≤ 1.0) to evaluate the effect of Sn doping on oxygen mobility of the materials. The corresponding results accompanied with the amount of released O₂ were displayed in Fig. 3.

For undoped BaFeO_{3-δ} sample, an intense desorption peak of O₂ (ca. 0.356 mmol/g) could be observed ranging from 340 °C to about 550 °C with the center locating at 446 °C, which was attributed to the cracking of Fe-O bond. When Sn cations were doped, it was clearly noticed that the amount of desorbed O₂ rapidly decreased with increasing the Sn content from 0.249 mmol/g for x = 0.2 sample to 0.033 mmol/g for x = 0.8 sample. For pure BaSnO₃ without any Fe cations (x = 1.0), the oxygen signal was not detected at all, which means the desorbed oxygen was derived from cracking of Fe-O bond while Sn-O bond was so strong that could not be easily broken under the conditions for O₂-TPD experiment (50 ~ 900 °C, He atmosphere). Besides, the capacity to release lattice oxygen (per mol Fe cations) for BaFe_{1-x}Sn_xO_{3-δ} catalysts also gradually reduced from 85 mmol_{O₂} mol_{Fe}⁻¹ for x = 0 sample to 48 mmol_{O₂} mol_{Fe}⁻¹ for x = 0.8 sample (Fig. S3), suggesting that

partial lattice oxygen surrounding Fe was stabilized after doping of Sn cations. However, it was interesting to notice that the onset temperature of O₂ desorption peak gradually shifted to lower temperature with increasing the Sn content (Fig. S4), which indicated that the oxygen mobility of BaFe_{1-x}Sn_xO_{3-δ} materials ($0 \leq x \leq 0.8$) was improved with increasing the Sn content. This result revealed that the Fe-O bond was probably weakened after doping of Sn cations, which should be responsible for the enhancement of their intrinsic rate (Fig. 1b).

The phase compositions of BaFe_{1-x}Sn_xO_{3-δ} samples after O₂-TPD experiment were also investigated to check the structure stability (Fig. S5). For $x = 0$ sample, the perovskite structure no longer existed and transformed to the monoclinic form (BaFeO_{2.5}) with ordered oxygen vacancies after losing part of lattice oxygen, which was proved to be detrimental to the oxygen mobility of the perovskite material ^[52]. This result indicated the unstable structure of BaFeO_{3-δ}, which greatly limited its application in redox heterogeneous catalysis. It was noteworthy that, unlike the $x = 0$ sample, all the Sn doped catalysts ($x = 0.2 \sim 1.0$) still retained the cubic perovskite structure (Fig. S5) after O₂-TPD experiment, implying the outstanding stabilization effect of Sn cations on the perovskite structure. Based on above analysis, it is reasonable to deduce that the enhanced structural stability and the improved oxygen mobility made these Sn doped materials good candidates for catalysts in redox reactions.

3.2.3. Identification of the chemical state of Fe and Sn in BaFe_{1-x}Sn_xO_{3-δ}

3.2.3.1. XPS

Fig. 4. Fitted Sn3p and Fe2p core-level photoemission spectra of $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ samples.

The chemical state of surface Sn and Fe cations in as-prepared $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ catalysts was investigated using XPS. The core-level Sn3p and Fe2p spectra were shown in Fig. 4 and the corresponding fitted results were summarized in Table 2. The Sn3p spectrum in all the samples could be well fitted by one singlet with the binding energy (B.E.) ranging from 715.3 to 715.6 eV. Such a feature was characteristic of Sn^{4+} [53]. The XPS region for Fe 2p showed a doublet, which was ascribed to the Fe 2p3/2 and 2p1/2, respectively. This doublet could be further deconvoluted into two subspectra centering at 710.4 ~ 710.8 eV and 712.4 ~ 712.8 eV, corresponding to the surface Fe^{3+} and Fe^{4+} cations, respectively [54, 55]. The shake-up locating at ca. 719 eV was attributed the satellite peak of Fe^{3+} cations [56]. From the above results, one can conclude that the as-prepared $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ samples contained both Fe^{3+} and Fe^{4+} cations at the surface of these samples. The formation of unusual tetravalent Fe cations has also been observed in perovskite oxides, such as $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ [54], $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{M}_y\text{O}_3$ ($\text{M} = \text{Bi}, \text{Co}$) [31, 57], $\text{Ba}_{1-x}\text{Nd}_x\text{FeO}_3$ [58] etc. The surface composition of these catalysts was estimated according to the fitted results. It was noticed that the surface composition was identical to that in the whole catalyst. To be noted, the $\text{Fe}^{4+}/\text{Fe}_{\text{total}}$ percentage showed an interesting volcano-shaped variation with a highest value of 27% for $x = 0.4$

sample as increasing Sn content from $x = 0$ to $x = 0.8$. Such trend indicated that doping of Sn in $\text{BaFeO}_{3-\delta}$ could adjust the chemical state of Fe cations in the perovskite matrix.

Table 2. XPS analysis of as-prepared $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ catalysts.^a

Samples	Binding energy, eV			Fe/Ba, ^a	Sn/Ba, ^a	O/Ba, ^a	Fe ⁴⁺ /Fe _{total} , ^b %
	Sn ⁴⁺	Fe ³⁺	Fe ⁴⁺				
$x = 0$	-	710.6	712.6	0.90	0	3.35	20
$x = 0.2$	715.3	710.4	712.8	0.73	0.23	3.56	23
$x = 0.4$	715.4	710.8	712.8	0.53	0.43	3.64	26
$x = 0.6$	715.5	710.6	712.5	0.38	0.62	3.40	19
$x = 0.8$	715.5	710.8	712.4	0.21	0.80	3.47	15
$x = 1.0$	715.6	-	-	0	1.23	3.30	-

^a Relative accuracy $\sim 20\%$.

^b Fe_{total} equals to the total amount of Fe³⁺ and Fe⁴⁺ cations.

3.2.3.2. ¹¹⁹Sn and ⁵⁷Fe Mössbauer spectroscopy

The chemical state of Sn and Fe cations in $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ matrix was further investigated by ¹¹⁹Sn and ⁵⁷Fe Mössbauer spectroscopy. Primary, two kinds of information could be obtained through this technique, namely isomer shift (IS) and quadruple splitting (QS). The IS value is sensitive to the valence state and atomic spacing, while the QS value is closely related to the symmetry of the charge surrounding the target atoms.

The ¹¹⁹Sn Mössbauer spectra for the as-prepared $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0.2 \leq x \leq 1.0$) catalysts and these samples after O₂-TPD analysis were shown in Fig. 5 and the corresponding fitted hyperfine parameters were given in Table 3. It was noticed that all the spectra (Fig. 5) could be well fitted by a single Lorentzian curve, indicating that Sn cations in these catalysts retained homogeneous and unique state.

Fig.5. Room temperature ^{119}Sn Mössbauer spectra of (a) as-prepared $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0.2 \leq x \leq 1.0$) catalysts and (b) samples after O_2 -TPD analysis.

Table 3. Room temperature ^{119}Sn Mössbauer parameters of $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0.2 \leq x \leq 1.0$) samples.^a

Samples	As-prepared			After O_2 -TPD experiment			Assignment
	IS, mm/s	QS, mm/s	A, ^b %	IS, mm/s	QS, mm/s	A, ^b %	
x = 0.2	0.08	0.35	100	0.08	0.42	100	$\text{Sn}^{4+}\text{-O}_6$
x = 0.4	0.06	0.32	100	0.05	0.38	100	$\text{Sn}^{4+}\text{-O}_6$
x = 0.6	0.03	0.12	100	0.03	0.14	100	$\text{Sn}^{4+}\text{-O}_6$
x = 0.8	0.01	0.04	100	0.01	0.05	100	$\text{Sn}^{4+}\text{-O}_6$
x = 1.0	0.00	0.00	100	0.00	0.00	100	$\text{Sn}^{4+}\text{-O}_6$

^a Experimental errors are ± 0.02 mm/s for isomer shift (IS), ± 0.03 mm/s for quadrupole splitting (QS) and 2% for relative area.

^b Relative area.

The IS values observed for all these samples lied in the range from 0.00 to 0.08 mm/s, which was characteristic of Sn^{4+} species ($4d^{10}5s^05p^0$, IS = $-0.4 \sim 2.0$ mm/s) [59, 60]. This result confirmed that Sn ions were exclusively in the +4 oxidation state. Taking both IS and QS parameters into account, the small values (IS = $0.00 \sim 0.08$ mm/s, QS = $0.00 \sim 0.42$ mm/s) were characteristic of the octahedral coordinated $\text{Sn}^{4+}\text{-O}_6$ (both IS and QS close to 0 mm/s) rather than defective $\text{Sn}^{4+}\text{-O}_5$ with one oxygen vacancy (generally QS > 0.7 mm/s, IS value > 0.3 mm/s) [61]. This result indicated that the Sn^{4+} cations in both as-prepared catalysts and the samples after O_2 -TPD experiment were all six-fold coordinated with the oxygen anion, which further confirmed the strong Sn-O interaction and

the oxygen liberated from the $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ samples ($x = 0 \sim 0.8$) in the O_2 -TPD experiment originated from the cracking of Fe-O bond.

For the minor doped $\text{BaFe}_{0.8}\text{Sn}_{0.2}\text{O}_{3-\delta}$ sample, the IS value of Sn cations was fitted to be 0.08 mm/s, larger than that of bulk BaSnO_3 (0.00 mm/s) and SnO_2 (-0.01 mm/s) ^[62], which means that the s electron density around Sn nuclei was increased for $x = 0.2$ sample ($\text{Sn/Fe} = 1/4$) ^[62]. In other words, the Sn cations was slightly reduced (compared to Sn in BaSnO_3 and SnO_2) after introduction into $\text{BaFeO}_{3-\delta}$. Further improving the Sn content from 0.4 ($\text{Sn/Fe} = 2/3$) to 0.8 ($\text{Sn/Fe} = 4/1$) resulted in reduction of IS value from 0.06 to 0.01 mm/s, indicating the gradually increase of the oxidation state of Sn cations, in good agreement with the XPS results (Fig. 4). For perovskite oxides with cubic structure, the A cations locate at the center of the cubic cell formed by B cations while the oxygen anions occupy the middle of the edges (Fig. S6a) ^[63]. As for $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ catalysts, the Fe-O-Sn structure would be inevitably formed when the Fe cations were partially replaced by Sn (Fig. S6b). The slightly lower oxidation state of Sn cations in $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ than that in BaSnO_3 may be attributed to the higher electronegativity of Sn cations than Fe, which made the Sn possessed stronger force to draw electrons from oxygen anions ^[64]. Such interaction between the B cations in perovskite oxides has also been observed in the partially B-site substituted LaMnO_3 and EuCoO_3 system by Pecchi et al. ^[65] and Wu et al. ^[32]. The chemical state of B-site cations in perovskite oxides was closely related to the B-O interaction. Therefore, one can expect that the chemical state of Fe would be changed with the Sn content in $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$, which would further alter the corresponding catalytic behavior of these materials.

Fig.6. Room temperature ^{57}Fe Mössbauer spectra of (a) as-prepared $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.8$) catalysts and (b) samples after O_2 -TPD analysis.

Table 4. Room temperature ^{57}Fe Mössbauer parameters of $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.8$) samples. ^a

Samples	As-prepared				After O_2 -TPD experiment					Assignment
	IS, mm/s	QS, mm/s	A, ^b %	δ^d	IS, mm/s	QS, mm/s	B, ^c T	A, ^b %	δ^d	
x = 0	-0.11	0.63	22	0.33	-	-	-	-	0.50 ^e	$\text{Fe}^{4+}\text{-O}_6$
	0.42	0.77	30		0.45	-0.15	50.7	14		$\text{Fe}^{3+}\text{-O}_6$
	0.31	0.77	30		0.37	-0.49	49.1	15		$\text{Fe}^{3+}\text{-O}_5$
	-	-	-		0.33	-0.63	47.3	13		$\text{Fe}^{3+}\text{-O}_5$
	-	-	-		0.23	0.51	43.0	15		$\text{Fe}^{3+}\text{-O}_4$
	0.14	0.80	18		0.15	-0.15	40.2	43		$\text{Fe}^{3+}\text{-O}_4$
x = 0.2	-0.08	0.66	25	0.25	-0.10	0.69	-	19	0.38	$\text{Fe}^{4+}\text{-O}_6$
	0.46	0.91	25		0.38	0.77	-	21		$\text{Fe}^{3+}\text{-O}_6$
	0.31	0.85	38		0.25	0.81	-	26		$\text{Fe}^{3+}\text{-O}_5$
	0.15	0.79	12		0.11	0.78	-	34		$\text{Fe}^{3+}\text{-O}_4$
x = 0.4	-0.05	0.59	29	0.15	-0.12	0.58	-	25	0.24	$\text{Fe}^{4+}\text{-O}_6$
	0.47	0.87	22		0.41	0.78	-	16		$\text{Fe}^{3+}\text{-O}_6$
	0.34	0.79	49		0.24	0.80	-	37		$\text{Fe}^{3+}\text{-O}_5$
	-	-	-		0.12	0.66	-	22		$\text{Fe}^{3+}\text{-O}_4$
x = 0.6	-0.04	0.68	23	0.12	-0.13	0.64	-	20	0.17	$\text{Fe}^{4+}\text{-O}_6$
	0.48	0.83	17		0.41	0.80	-	14		$\text{Fe}^{3+}\text{-O}_6$
	0.34	0.82	60		0.25	0.79	-	47		$\text{Fe}^{3+}\text{-O}_5$
	-	-	-		0.11	0.69	-	19		$\text{Fe}^{3+}\text{-O}_4$
x = 0.8	-0.03	0.59	16	0.07	-0.07	0.83	-	14	0.09	$\text{Fe}^{4+}\text{-O}_6$
	0.59	0.16	16		0.54	0.78	-	12		$\text{Fe}^{3+}\text{-O}_6$

0.39	0.82	68	0.34	0.77	-	62	Fe ³⁺ -O ₅
-	-	-	0.12	0.85	-	13	Fe ³⁺ -O ₄

^a Experimental errors are ± 0.02 mm/s for isomer shift (IS), ± 0.03 mm/s for quadrupole splitting (QS) and 2% for relative area.

^b Relative area.

^c Hyperfine magnetic field.

^d δ is calculated based on the Mössbauer results.

^e Data from reference 27.

The room temperature ⁵⁷Fe Mössbauer spectra for as-prepared BaFe_{1-x}Sn_xO_{3- δ} ($0 \leq x \leq 0.8$) were shown in Fig. 6a and the corresponding fitted parameters were presented in Table 4. According to the literature [66-68], the high spin Fe²⁺ (3s²3p⁶3d⁶), Fe³⁺ (3s²3p⁶3d⁵) and Fe⁴⁺ (3s²3p⁶3d⁴) cations displayed different IS values of 0.6 ~ 1.7, 0.1 ~ 0.6, and -0.2 ~ 0.2 mm/s, respectively. Comparing the IS values (-0.11 ~ 0.59 mm/s) listed in Table 4, Fe ions in the BaFe_{1-x}Sn_xO_{3- δ} catalysts existed in tetravalent (Fe⁴⁺) or trivalent (Fe³⁺) oxidation state. Unlike the XPS analysis (Fig. 4), where only Fe³⁺ and Fe⁴⁺ were distinguished, the spectrum of the x = 0 sample (Fig. 6a) could be deconvoluted into four subspectra, indicating that four kinds of Fe species with different valence states or coordination conditions coexisted in the as-prepared BaFeO_{3- δ} . These doublets with IS values of -0.11, 0.42, 0.30 and 0.14 mm/s (Table 3) were assigned to octahedral coordinated Fe⁴⁺ (Fe⁴⁺-O₆), octahedral coordinated Fe³⁺ (Fe³⁺-O₆), tetragonal pyramidal coordinated Fe³⁺ (Fe³⁺-O₅ with one adjacent oxygen vacancy) and tetrahedral coordinated Fe³⁺ (Fe³⁺-O₄ with two adjacent oxygen vacancies), respectively [69, 70]. The proportion of Fe⁴⁺ (Fe⁴⁺-O₆) and Fe³⁺ species (Fe³⁺-O₆, Fe³⁺-O₅, Fe³⁺-O₄) were 22% and 78%, respectively, in good agreement with the XPS results (Table 2).

For Sn doped samples ($0.2 \leq x \leq 0.8$), the IS values of these four doublets all slightly increased with the Sn content. Such result indicated that introduction of Sn into BaFeO_{3- δ} resulted in weakening of Fe-O interaction and lowering the valence state of Fe cations, which should be attributed to the extended Fe-O bond caused by cell volume expansion (Table 1) and formation of

Fe-O-Sn structure. As for the relative area (A) of these four Fe species, it was interesting that the variation tendency with increasing the Sn content differed a lot from each other. The amount of Fe^{4+} (Table 4) was volcano-shaped, with a maximum value of 29% for $x = 0.4$ sample. In contrast, the percentage of $\text{Fe}^{3+}\text{-O}_6$ (30% for $x = 0$ to 16% for $x = 0.8$) and $\text{Fe}^{3+}\text{-O}_4$ (18% for $x = 0$ to 0% for $x \geq 0.4$) species was gradually declined while that of $\text{Fe}^{3+}\text{-O}_5$ groups was noticed to be progressively increased (30% for $x = 0$ and 68% for $x = 0.8$). The above results demonstrated that the doping of Sn in $\text{BaFeO}_{3-\delta}$ not only influenced the valence state of Fe cations, but also significantly adjust their coordination conditions, both of which were closely related to the catalytic performance of Fe cations.

After O_2 -TPD analysis (Fig. 6b), the ^{57}Fe Mössbauer spectrum of $x = 0$ sample showed overlay of five sextets rather than doublet patterns, indicating the dramatically changed structure of this catalyst due to the desorption of lattice oxygen. The five sextets were assigned to five different Fe^{3+} species and the corresponding hyperfine parameters (Table 4) were in good agreement with the fitted parameters for monoclinic $\text{BaFeO}_{2.5}$ by Clemens et al. [27]. In contrast, the spectra of Sn doped samples ($x = 0.2 \sim 0.8$) still showed overlay of four paramagnetic doublet patterns after the O_2 -TPD experiment. This result further confirmed that formation of Fe-O-Sn structure could effectively stabilize the structure of the $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($x = 0.2 \sim 0.8$) catalysts.

4. Discussion

4.1. Effect of Sn doping on the stability of perovskite structure

The stability of perovskite structure was closely related to the concentration of oxygen vacancies, and the perovskite matrix would be destroyed once ordered oxygen vacancies were formed [41, 71]. For $x = 0$ sample, the percentage of coordinately unsaturated Fe cations increased from 48% (30%

for $\text{Fe}^{3+}\text{-O}_5$, 18% for $\text{Fe}^{3+}\text{-O}_4$, Table 4) to 86% (28% for $\text{Fe}^{3+}\text{-O}_5$, 58% for $\text{Fe}^{3+}\text{-O}_4$, Table 4) during the O_2 -TPD experiment, indicating that large amount of oxygen vacancies was generated. The concentration of oxygen vacancies ($\delta = 0.50$) was so high that resulted in the collapse of $\text{BaFeO}_{3-\delta}$ perovskite matrix and the structural transformation from rhombohedral to monoclinic form. Upon introducing the Sn cations into $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($x = 0.2 \sim 1.0$), the oxygen anions adjacent to Sn could be well stabilized even in inert atmosphere at temperature as high as 900 °C due to the strong Sn-O interaction, which led to reduction of the oxygen vacancies and formation of cubic perovskite structure. As a consequence, the stability of the perovskite structure was significantly improved after doping of Sn cations.

4.2. Effect of Sn doping on the oxygen mobility

The oxygen mobility of perovskite catalysts was determined by the B-O bond ^[72]. Generally, weaker B-O bond would lead to easier removal of the oxygen coordinated with B cations ^[73-75]. For $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0.2 \leq x \leq 0.8$) catalyst with cubic perovskite structure (Fig. S6b), three different kinds of B-site interaction, including Fe-O-Fe, Fe-O-Sn and Sn-O-Sn, were expected to coexist in the perovskite matrix. With increasing the Sn content, the theoretical percentage of the three different interactions changed simultaneously (Table S1). As for the oxygen anions involved in Fe-O-Sn and Sn-O-Sn, they were expected to exhibit low mobility as a result of strong Sn-O bond. This conclusion was supported by the result of ¹¹⁹Sn Mössbauer analysis (Table 3) that all Sn cations were 6-fold coordinated with oxygen anions. In contrast, the oxygen in Fe-O-Fe species should be more mobile because of the relatively weaker Fe-O bond (compared to Sn-O bond) ^[72, 76]. Yildiz et al.^[77] also found in their experiments that doping of less reducible cations (e.g. Hf^{4+} , Zr^{4+} and Al^{3+}) in $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ would suppress the formation of oxygen vacancies by formation of B-O-Co structure

(B represents the doped cations), since the bonding energy of B-O is much stronger than Co-O bond. When the Fe cations in BaFeO_{3-δ} were partially replaced by larger Sn with higher electronegativity, the Fe-O bond was elongated (Table 1) and valence state of Fe cations were gradually reduced as evidenced by ⁵⁷Fe Mössbauer analysis (Table 4), which notably weakened the interaction between Fe cations and adjacent oxygen anions [78, 79]. As a result, doping of Sn in BaFeO_{3-δ} can enhance the oxygen mobility of the catalyst.

Actually, the oxygen (not adjacent to Sn) in different trivalent Fe species (Fe³⁺-O₆, Fe³⁺-O₅ and Fe³⁺-O₄) also exhibited distinct mobility due to the rather different Fe-O bond strength even if the Sn content was constant, which means these Fe species may contribute differently to N₂O decomposition. The strength of Fe-O interaction followed the order: Fe³⁺-O₆ < Fe³⁺-O₅ < Fe³⁺-O₄, judging from the corresponding IS values (Table 4) of ca. 0.4 mm/s, 0.25 mm/s and 0.12 mm/s, respectively. Besides, it was found from the ⁵⁷Fe Mössbauer results (Table 4) that the percentage of Fe³⁺-O₆ and Fe³⁺-O₅ species was lowered after O₂-TPD treatment while that of Fe³⁺-O₄ greatly increases. This result indicates that part of Fe³⁺-O₆ and Fe³⁺-O₅ is converted to Fe³⁺-O₄ in this process by breaking of Fe-O bond. Therefore, a reverse trend of oxygen mobility could be predicted for these four Fe species. In other words, the oxygen confined in Fe³⁺-O₆ and Fe³⁺-O₅ species was easier to be released than that in Fe³⁺-O₄.

4.3. Effect of Sn doping on chemical state of Fe

As mentioned above, the chemical state of Fe, which determined the N₂O decomposition performance, was spontaneously altered with the content of Sn cations. Basically, doping of Sn cations induced two different changes in BaFe_{1-x}Sn_xO_{3-δ} (x = 0.2 ~ 0.8) system: (1) weakening of Fe-O bond due to expansion of cell volume and formation of Fe-O-Sn structure; (2) reduction of the

oxygen vacancies. These two different changes exhibited competitive effect on the valence of Fe cations. For the catalysts with low Sn content ($x = 0.2$ and 0.4), the charge compensate effect caused by the reduction of oxygen vacancies was predominant, which resulted in increase of Fe^{4+} percentage from 22% for $x = 0$ sample to 29% for $x = 0.4$ sample (Table 4). Further improve the Sn loading to $x = 0.6$ and 0.8 , weakening of Fe-O interaction was overwhelming, which led to increase of d electron density of Fe cations and reduction of the $\text{Fe}^{4+}/\text{Fe}^{3+}$ ratio.

Besides the valence state, the coordination condition of the Fe^{3+} cations was also greatly changed due to doping of Sn cations (Table 4). Increasing the Sn content resulted in the Fe cations being surrounded by more Sn with the formation of Fe-O-Sn structure. Therefore, more oxygen anions adjacent to Fe cations were fixed in Fe-O-Sn structure, which made the simultaneous appearance of two oxygen vacancies around single Fe cation ($\text{Fe}^{3+}\text{-O}_4$) to be difficult and reduced $\text{Fe}^{3+}\text{-O}_4$ groups in the as-prepared catalysts (18% for $x = 0$ and 0% for $x = 0.4 \sim 0.8$ samples). On the other hand, the oxygen involved in Fe-O-Fe structure was more prone to be removed after introduction of Sn in $\text{BaFeO}_{3-\delta}$ due to the gradually weakened Fe-O interaction. Such feature resulted in the decline of coordinatively saturated $\text{Fe}^{3+}\text{-O}_6$ groups (30% for $x = 0$ to 16% for $x = 0.8$ sample). As a result, the percentage of $\text{Fe}^{3+}\text{-O}_5$ was notably improved (30% for $x = 0$ to 68% for $x = 0.8$ sample) with the Sn content (Table 4). On the whole, the percentage of coordinately unsaturated Fe species ($\text{Fe}^{3+}\text{-O}_5$ and $\text{Fe}^{3+}\text{-O}_4$), which was generally accepted as the sites for N_2O adsorption and activation^[23, 51, 80], was improved from 48% (referred to total Fe content) for $x = 0$ to 68% for $x = 0.8$ sample.

4.4. Effect of Sn doping on N_2O decomposition

For N_2O decomposition, the desorption of oxygen from catalyst surface is regarded as the tardy step^[51, 80]. Therefore, the reaction order of N_2O decomposition with respect to O_2 was measured to

investigate the effect of Sn doping on the performance of $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.8$) catalysts. The result was showed in Fig. 7. The negative apparent reaction orders ($-0.47 \sim -0.2$) indicated the competing adsorption of O_2 and N_2O on the Fe active centers. However, it was obvious that the influence of O_2 differed a lot with the Sn content. For pure $\text{BaFeO}_{3-\delta}$ sample, an order of -0.47 was observed, which was close to the value of -0.50 for rare-earth oxides^[81]. This result suggested that there existed strong competitive adsorption between O_2 and N_2O molecules on Fe active centers of $\text{BaFeO}_{3-\delta}$ catalyst due to the strong Fe-O interaction and relatively low lattice oxygen mobility. For Sn doped samples, it was found that the reaction order gradually increased with the Sn content (-0.39 for $x = 0.2$ sample and -0.20 for $x = 0.8$ sample), indicating the lowered inhibitory effect of O_2 . By contrast, the reaction order with respect to N_2O almost remains unchanged (around 1.0) with increasing the Sn content (Fig. S7). The above results suggested that the notably increased intrinsic rate for N_2O decomposition over $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.8$) catalysts should be mainly attributed to the accelerated oxygen desorption from Fe active centers induced by doping of Sn cations.

Fig. 7. Apparent reaction orders of O_2 for N_2O decomposition on $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.8$) catalysts. Feed: 10% N_2O , 10% N_2 , 5 - 20% O_2 , and Ar balance. Temperature: 590 °C for $x = 0.8$ and 0.6 ; 610 °C for $x = 0.4$, 0.2 and 0 . Experimental errors for the O_2 order are ± 0.02 .

4.5. Active center for N_2O decomposition

It was generally accepted that the active centers for N₂O decomposition over transition metal oxides were assigned to the coordinatively unsaturated cations [23]. As for BaFe_{1-x}Sn_xO_{3-δ} (0 ≤ x ≤ 0.8) catalysts, the Fe³⁺-O₅ and Fe³⁺-O₄ species could both act as N₂O adsorption centers due to their coordinatively unsaturated feature. To confirm the dominant active centers for N₂O decomposition, a correlation between the percentage of different Fe species and the intrinsic rate was intuitively expounded in Fig. 8. For x = 0 sample, the percentage of Fe³⁺-O₅ was only 30% while the Fe³⁺-O₄ cations were ca. 18%, and the intrinsic rate was calculated to be ca. 0.43 s⁻¹. When the Sn content was increased, the ratio of Fe³⁺-O₄ was lowered until completely disappeared for x ≥ 0.4 samples, while the percentage of Fe³⁺-O₅ was gradually increased, accompanied by the improved reaction rate. In particular, when x reached 0.8, which showed the largest concentration of Fe³⁺-O₅ (68%), the highest normalized rate of 1.49 s⁻¹ was obtained. The variation trend between percentage of Fe³⁺-O₅ and the TOF values is similar, although the amplitude of variation is a little different, which may be induced by the changed oxygen mobility and the contribution of Fe³⁺-O₄ to the catalytic process. The above results strongly suggested the Fe³⁺ ions that five-fold coordinated with oxygen (Fe³⁺-O₅) should account for the active sites for N₂O decomposition.

Fig. 8. Variation of the intrinsic rate for N₂O (30 vol% N₂O in Ar) decomposition at 550 °C vs the percentage of different Fe species as a function of Sn content in BaFe_{1-x}Sn_xO_{3-δ} (0 ≤ x ≤ 0.8).

To double check this conclusion, a proof test was carried out as follows: the x = 0.2 catalyst was treated as the procedure for O₂-TPD experiment to release partial lattice oxygen and then reused for N₂O (30 vol%) decomposition, where the reaction was performed at 550 °C for 0.5 h. The catalyst after the reaction was characterized by ⁵⁷Fe Mössbauer spectroscopy as displayed in Fig. 9, and the corresponding fitted parameters were listed in Table 5.

Fig. 9. Room temperature ⁵⁷Fe Mössbauer spectrum of the BaFe_{0.8}Sn_{0.2}O_{3-δ} catalyst after O₂-TPD experiment and subsequent catalytic reaction for N₂O decomposition (30 vol%) at 550 °C for 0.5 h.

Table 5. Room temperature ⁵⁷Fe Mössbauer parameters of the BaFe_{0.8}Sn_{0.2}O_{3-δ} catalyst after O₂-TPD experiment and subsequent reaction for N₂O decomposition.^a

Treatment	IS, mm/s	QS, mm/s	A, ^b %	Assignment
N ₂ O reaction	-0.09	0.75	21	Fe ⁴⁺ -O ₆
	0.36	0.77	22	Fe ³⁺ -O ₆
	0.27	0.85	30	Fe ³⁺ -O ₅
	0.11	0.82	27	Fe ³⁺ -O ₄

^a Experimental errors are ± 0.02 mm/s for isomer shift (IS), ± 0.03 mm/s for quadrupole splitting (QS) and 2% for relative area.

^b Relative area.

For the BaFe_{0.8}Sn_{0.2}O_{3-δ} catalyst after O₂-TPD experiment (Fig. 6 and Table 4), Fe species was consisted of 20% Fe⁴⁺-O₆, 21% Fe³⁺-O₆, 25% Fe³⁺-O₅, and 34% Fe³⁺-O₄. When the catalyst was exposed to the feed gas (N₂O and a small amount of generated O₂ by N₂O decomposition), the

percentage of $\text{Fe}^{3+}\text{-O}_4$ reduced to 27% from 34% (Table 5), while that of $\text{Fe}^{3+}\text{-O}_5$ increased to 30% from 25%. This result indicated that the $\text{Fe}^{3+}\text{-O}_4$ center could strongly stabilized the adsorbed oxygen generated by N_2O decomposition and subsequently be partially converted to $\text{Fe}^{3+}\text{-O}_5$. In contrast, the oxygen adsorbed on $\text{Fe}^{3+}\text{-O}_5$ site can be quickly released thanks to the relatively weaker Fe-O interaction, which was confirmed by the fact that the percentage of $\text{Fe}^{4+}\text{-O}_6$ and $\text{Fe}^{3+}\text{-O}_6$ almost remained unchanged after the reaction. This conclusion was also supported by the corresponding catalytic result (Fig. S8) that the conversion of N_2O (represented by O_2 signal) slightly increases during the reaction of initial several minutes, which should be attributed to the increased $\text{Fe}^{3+}\text{-O}_5$ species. Based on above analysis, one can conclude that the $\text{Fe}^{3+}\text{-O}_5$ species were the main active centers for N_2O decomposition. Therefore, the increased TOF values for N_2O decomposition with the Sn content (Fig. 8) should be assigned to both the enhanced oxygen mobility and improved percentage of active $\text{Fe}^{3+}\text{-O}_5$ (in total Fe) species from 30% for $x = 0$ to 68% for $x = 0.8$ sample.

Fig. 10. Possible mechanism for N_2O decomposition on $\text{Fe}^{3+}\text{-O}_5$ active site in $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.8$) catalysts. “□” stands for the oxygen vacancy.

Based on above analysis, The possible process for N_2O decomposition occurred on the $\text{BaFe}_{1-x}\text{Sn}_x\text{O}_{3-\delta}$ catalysts is displayed in Fig. 10. First, the N_2O molecules adsorbs on the coordinatively unsaturated $\text{Fe}^{3+}\text{-O}_5$ with the formation of N_2 and adsorbed oxygen. Subsequently, this adsorbed monoatomic O oxygen desorbs either by the reaction of an adsorbed monoatomic oxygen

with the N₂O (route I), or by recombination of two adjacent oxygen atoms (route II).

5. Conclusion

In summary, the effect of Sn doping on chemical state of Fe in BaFe_{1-x}Sn_xO_{3-δ} was systematically investigated, and it was found that there existed synergistic effect between Fe and Sn, which explained the different catalytic behavior of these catalysts for N₂O decomposition. The Fe³⁺-O₅ species in BaFe_{1-x}Sn_xO_{3-δ} (0 ≤ x ≤ 0.8) catalysts accounted for the main active centers for the reaction. Doping of Sn in BaFeO_{3-δ} catalyst notably increased the percentage of Fe³⁺-O₅ active centers from 30% (x = 0) to 68% (x = 0.8). More importantly, substitution of Fe by Sn cations could lower the valence state of Fe, since the Fe-O bond was stretched due to formation of Fe-O-Sn structure and expansion of cell volume. As a result, the Fe-O interaction was weakened and oxygen mobility of the catalyst was greatly improved, which led to the reduction of activation energy for N₂O decomposition from ca. 241 kJ mol⁻¹ (x = 0) to 178 kJ mol⁻¹ (x = 0.8). BaFe_{0.2}Sn_{0.8}O_{3-δ} catalyst exhibited the highest intrinsic rate of 1.49 s⁻¹ (550 °C), nearly 4 times larger than BaFeO_{3-δ} (0.43 s⁻¹).

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Graphical Abstract

A series of structural changes of $\text{BaFeO}_{3-\delta}$ induced by the Sn doping and the connection with the N_2O catalytic decomposition activity were discussed at the molecule level.