制备方法对 $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ 钙钛矿型氧化物催化 甲烷燃烧反应性能的影响

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摘要: 分别采用甘氨酸硝酸盐法、溶胶凝胶法、共沉淀法、燃烧法以及水热法制备了钙钛矿型 $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ 复合氧化物, 用 X 射线衍射、红外光谱、 H_2 程序升温还原和低温 N_2 吸附对其进行了表征, 并考察了其对于甲烷燃烧的催化活性. 结果表明, 制备方法和焙烧温度对 $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ 钙钛矿型催化剂的结构、晶粒大小和不同类型的氧物种影响很大. 以甘氨酸硝酸盐法制备的钙钛矿型催化剂经 700°C 焙烧后表现出最高的催化活性, T_{50} (甲烷转化率达到 50% 时的温度) 仅为 440°C . 这归结于它较小的晶粒尺寸 (12.4 nm) 和较大的比表面积 ($18.6\text{ m}^2/\text{g}$), 以及催化剂表面富集的 Mn^{4+} , 从而使表面氧物种更容易移动和/或更具有反应活性.

关键词: $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$; 钙钛矿型催化剂; 制备方法; 焙烧温度; 甲烷燃烧

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Effects of Preparation Methods on the Catalytic Performance of $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ Perovskite for Methane Combustion

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Abstract: A perovskite-type composite oxide, $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$, was prepared by five methods, i.e., glycine-nitrate, sol-gel, co-precipitation, combustion synthesis, and hydrothermal treatment. The composites were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, H_2 -temperature-programmed reduction, and N_2 adsorption-desorption isotherms. The catalytic activity of $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ toward methane combustion was evaluated. The results show that the different preparation methods and calcination temperatures greatly influence the textural structure, crystallite size, and different oxygen species within the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ perovskite material. The perovskite catalyst synthesized by the glycine-nitrate method and calcined at 700°C shows the best activity for methane combustion among the tested materials. Its T_{50} (the reaction temperature at which 50% CH_4 is converted) is only $\sim 440^\circ\text{C}$. This good catalyst performance can be attributed to the small crystallite size (12.4 nm), larger surface area ($18.6\text{ m}^2/\text{g}$), and high concentration of surface Mn^{4+} cations, which creates more flexible and reactive surface oxygen species.

Key words: $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$; perovskite catalyst; preparation method; calcination temperature; methane combustion

As a novel catalytic and electronic material, perovskite composite oxides (general formula ABO_3) are being extensively researched, especially for the development of combustion catalysts and environmental purification catalysts. In the perovskite structures oxides such as the lanthanum manganites attract wide interest because of their unique

properties such as their catalytic activity in the total oxidation of methane, which is largely related to the high availability of lattice oxygen due to the presence of a considerable amount of Mn^{4+} (about 35%) in addition to Mn^{3+} [1]. Moreover, the stable structure of the perovskites allows for the partial substitution of A and/or B by other metals (tran-

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sition or rare metal ions), which can improve the perovskite structure or its properties. La-Ce-Mn-O-perovskite has been studied and it has been found that partial substitution of lanthanum by cerium can improve the redox property and stability of the oxygen species on the surface of the perovskite catalyst resulting in improved catalytic activity during methane combustion [2]. Substitution with lower valence cations forces the B-element into a higher oxidation state or allows the formation of oxygen vacancies, which leads to an improvement in catalytic activity [3]. Saracco et al. [4] studied the partial substitution of B sites in $\text{LaMn}_{1-x}\text{Mg}_x\text{O}_3$ ($x = 0-0.5$) with Mg and found that adding Mg can force a large portion of the Mn^{3+} to oxidize to Mn^{4+} to balance the total charge in the materials. The presence of M^{4+} cations in $\text{LaMn}_{1-x}\text{Mg}_x\text{O}_3$ can enhance the catalytic activity by influencing the active lattice oxygen near the Mn^{4+} that takes part in methane oxidation.

Because of the high catalytic activities of the substituted perovskites, many studies on the effect of their physico-chemical and catalytic properties have been done recently. These studies included their composition and preparation methods, and it is obvious that the effect of the preparation method on the properties of substituted perovskite materials is of great importance. Using different preparation routes and technical conditions such as a solid-state reaction, sol-gel, hydrothermal treatment, spray-drying, freeze-drying, co-precipitation, chemical vapor deposition, and microemulsion, substituted perovskite materials with different surface and structural properties have been prepared [5]. Ifrah et al. [6] compared the conventional hydrothermal process with microwave-assisted hydrothermal synthesis when preparing the $\text{La}_{1-x}\text{Ag}_x\text{MnO}_{3+\delta}$ perovskite catalysts for methane combustion and found that the surface physico-chemical properties of the catalysts were strongly influenced by the preparation method. They also studied the effect of the type of oxygen species (including amount and mobility) on their catalytic properties for methane combustion. Gosavi et al. [7] studied the synthesis of the LaFeO_3 perovskite by co-precipitation, combustion, and sol-gel methods and discovered that the perovskite synthesized by the sol-gel method yields a comparatively pure single crystalline phase of LaFeO_3 with a relatively higher surface area and porosity.

In this paper, $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ perovskite materials were prepared by five different methods, namely glycine-nitrate, sol-gel, co-precipitation, combustion, and hydrothermal methods. The effects of preparation methods and calcination temperature on the physicochemical properties and the catalytic activity of the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ perovskite for methane combustion were studied by X-ray diffraction (XRD), N_2 adsorption-desorption isotherms, Fourier transform infrared spectroscopy (FT-IR), and H_2 -temperature-

programmed reduction (H_2 -TPR). We discuss the relationship between the synthesis method, structure, and surface properties as well as the catalytic activity for methane combustion.

1 Experimental

1.1 Catalyst preparation

1.1.1 Glycine-Nitrate method (GN) [8]

Stoichiometric amounts of lanthanum, magnesium, and manganese nitrates were dissolved in deionized water to create synthesis solution A. This solution was followed by adding glycine ($\text{C}_2\text{H}_5\text{NO}_2$, La/glycine molar ratio = 3/8) to form a transparent solution. The solution was heated to 120 °C under vigorous stirring until all the water evaporated and a viscous material was obtained. After burning and a bright flame, a large amount of gases were observed and a puffy black powder was obtained.

1.1.2 Sol-gel method (SG) [9]

A certain amount of citrate acid (CA, La/CA molar ratio = 1/3) was added to synthesis solution A to form a transparent solution. Its pH was adjusted to 6–7 using 25% $\text{NH}_3\cdot\text{H}_2\text{O}$, and it was aged at 80 °C for about 3 h under vigorous stirring and then dried at 100 °C overnight.

1.1.3 Co-precipitation method (CP) [10]

As a precipitator, 1 mol/L 50 mol% $\text{NaOH-Na}_2\text{CO}_3$ aqueous solution was added dropwise to synthesis solution A while stirring until pH = 9–10. After the resulting suspension was left for 3 h, the precipitate was filtered and thoroughly washed 4–5 times with deionized water and ethanol to eliminate nitrate impurities and then the sample obtained was dried at 110 °C overnight.

1.1.4 Combustion synthesis (CS) [11]

Urea (La/urea molar ratio = 1/4.17) was added to synthesis solution A and it was heated to 90 °C on a hot plate until the water evaporated to obtain a viscous transparent material. This material was then heated in a muffle furnace to about 300 °C resulting in nitrate decomposition upon which a black powder was obtained.

1.1.5 Hydrothermal synthesis (HS)

Hexadecyl trimethyl ammonium bromide (CTAB) was dissolved in 50 ml deionized water to form solution B. So-

lution A was mixed with solution B to obtain a molar ratio of La/CTAB of 1/1.5. Urea (La/urea molar ratio = 1/5) was then added to the mixture under vigorous stirring for 3–4 h. The mixture was then transferred to a 100 ml Teflon-lined autoclave and hydrothermally treated at 80 °C for 24 h. The formed solid precursors were filtered and washed with de-ionized water and dried at 100 °C overnight.

The prepared samples were calcined in a muffle furnace at 600, 700, and 850 °C for 2 h in flowing air. After calcination, the solid powder was pressed and crushed to 40–60 mesh for characterization and activity testing.

1.2 Catalyst characterization

Wide-angle power XRD patterns were obtained on a Rigaku D/max 2250VB/PC diffractometer (Rigaku, Japan) using Cu K_{α} radiation ($\lambda = 0.154\ 06\ \text{nm}$). The average crystallite size of the catalyst was evaluated based on XRD peak broadening using the Scherrer equation $D = 0.9\lambda/\beta\cos\theta$, where λ is the radiation wavelength (0.154 05 nm) of Cu K_{α} , β is the half-width of the peak, and θ is the Bragg diffraction peak angle.

N₂ adsorption-desorption isotherms were measured at –196 °C on a NOVA 4200e surface area and pore size analyzer. Before measurement, the sample was outgassed at 180 °C under vacuum for 4 h. The surface areas of the samples were calculated by the Brumauer-Emmett-Teller (BET) method. FT-IR absorption spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer with 32 scans at an effective resolution of 4 cm^{–1}. The sample to be measured was ground with KBr and pressed into a thin wafer for analysis. H₂-TPR testing was conducted with a TCD detector. A 0.5 g sample was loaded into a U-shaped quartz tube reactor. A 5% H₂-95% N₂ gas mixture at 45 ml/min was used and the heating rate was 10 °C/min.

1.3 Catalytic activity testing

The catalytic performance of the LaMn_{0.8}Mg_{0.2}O₃ perovskite materials for methane combustion was carried out in a quartz tube microreactor ($\varnothing\ 6\ \text{mm}$) at atmospheric pressure. The reactor was placed in an electric furnace equipped with K-type thermocouples and temperature controllers. The reagent gas consisted of 1.0% CH₄-4.0% O₂-95% Ar, and its flow rate was 50 ml/min. The catalyst loading was 0.1 g and the weight hourly space velocity (WHSV) was 30 000 ml/(g·h). The reactants and products were analyzed by an online gas chromatograph (GC 8810) equipped with a column packed 5A molecular sieve and a thermal conductivity detector (TCD). Catalyst activity was evaluated using a temperature programmed mode from 200 to 700 °C at a heating rate of 5 °C/min.

2 Results and discussion

2.1 Textural properties

XRD patterns of the LaMn_{0.8}Mg_{0.2}O₃ prepared by different methods and calcined at different temperatures are given in Fig. 1. The XRD results show that a perovskite type structure was formed in all four samples prepared by the four different methods except for hydrothermal synthesis. Although the Mg content was as high as 20%, the perovskite structure remained intact and this is attributed to the presence of Mn⁴⁺ cations with a small ionic radius ($5.4 \times 10^{-2}\ \text{nm}$). This compensates for the steric and electronic effects of Mg-doping [4]. The results in Fig. 1(a) show that in the samples calcined at 600 °C the diffraction peaks of an impure phase (Mn₃O₄) are present at $2\theta = 29.7^\circ$ and 42.3° in addition to the diffraction peaks of the perovskite. After

Fig. 1. XRD patterns of the LaMn_{0.8}Mg_{0.2}O₃ catalysts prepared by different methods and calcined at 600 (a), 700 (b), and 850 °C (c).

calcination of the samples at 700 °C, the diffraction peaks of the perovskite strengthen obviously, and no impurity diffraction peaks are present. By increasing the calcination temperature to 850 °C, even more intensive diffraction peaks of the perovskites appear, which means that a decrease of amorphous materials takes place by crystallization and the crystal size of the perovskite increases. The sample prepared by HS appears to contain a phase of lanthanum oxide carbonate $\text{La}_2\text{O}_2\text{CO}_3$ after calcination at 600 °C and a mixed phase of lanthanum oxide carbonate ($\text{La}_2\text{O}_2\text{CO}_3$, La_2CO_3) as well as lanthanum hydroxide $\text{La}(\text{OH})_3$ after calcination at 700 °C. After it was calcined at 850 °C, lanthanum oxide La_2O_3 and lanthanum hydroxide $\text{La}(\text{OH})_3$ were present as was a trace of a LaMnO_3 perovskite phase.

The average crystallite sizes of the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ catalysts were calculated according to XRD peak broadening by the Scherrer equation and are shown in Table 1. The results show that the crystallite sizes of the samples calcined at 700 °C are smaller than those of the samples calcined at either 600 or 850 °C. An explanation for the above-mentioned phenomenon could be that the perovskite-like material only forms at an appropriate temperature. At the lower calcination temperature (600 °C), poorly crystalline and even an impurity of LaMnO_3 formed and at a higher calcination temperature (850 °C) sintering occurred and resulted in crystal growth. Therefore, the appropriate calcination temperature is 700 °C for the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ perovskite as a pure perovskite phase with relatively small crystal sizes was obtained after calcination at 700 °C. Among the four studied perovskite samples, the sample prepared by GN has the smallest crystal size and the crystal sizes increase in the order $\text{GN} < \text{SG} < \text{CP} < \text{CS}$. The difference in the crystallite sizes of the samples is due to the different formation mechanisms of crystal grains in the four preparation methods.

Based on the different preparation methods, samples with different surface areas were obtained. The results listed in Table 1 show that with an increase in calcination temperature from 600 to 850 °C, the surface areas of the samples decrease except for the sample prepared by CS. For instance, the surface area of the sample prepared by the

sol-gel method decreases from 25.3 to 12.6 m^2/g and the surface area of the sample synthesized by the co-precipitation method decreases from 28.0 to 15.7 m^2/g . The surface area of the sample prepared by combustion synthesis, after calcination at 700 °C, is larger than those calcined at 600 or 850 °C. Among the four perovskite samples, the surface area and crystal size of the sample prepared by GN varied little when the calcination temperature was increased from 600 to 850 °C, which indicates its high thermal stability.

Based on the above-mentioned results, the best calcination temperature for the synthesis of the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ perovskite material is 700 °C.

Figure 2 shows the FT-IR spectra of the prepared samples after calcination at 700 °C. The strong band at 620 cm^{-1} corresponds to the asymmetrical stretching vibration of the B–O bonds in the octahedron structure of BO_6 [12], which are the most important bonds in the perovskite structure. The band at 850 cm^{-1} can be assigned to $\nu_s(\text{COO})$, which shows that the surface carbonate groups are stable after calcination at 700 °C. The broad band at 3410 cm^{-1} and the small band at 1630 cm^{-1} are assigned to the stretching vibration of the O–H bond ($\nu_{\text{O-H}}$) and bending vibration of the H–O–H bond ($\nu_{\text{H-O-H}}$) of water. These are present because of sample exposure to air and environmental humidity. In

Fig. 2. FT-IR spectra of the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ catalysts prepared by different methods and calcined at 700 °C.

Table 1 BET surface areas and crystal sizes of the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ catalysts prepared by different methods and calcined at 600, 700, and 850 °C

Sample	BET surface area (m^2/g)			Crystal size (nm)		
	600 °C	700 °C	850 °C	600 °C	700 °C	850 °C
GN	20.8	18.6	17.0	13.6	12.4	13.9
SG	25.3	16.1	12.6	14.4	13.8	15.8
CP	28.0	19.8	15.7	16.7	15.1	15.5
CS	6.0	9.9	5.1	16.9	16.8	17.0
HS	20.7	26.4	20.4	—	—	—

Fig. 2(b), the broad bands centered at 1 481 and 1 385 cm^{-1} are assigned to vibration absorptions of the CO_3^{2-} anion ($\nu_{\text{as}}(\text{COO})$). The narrow band at 1 380 cm^{-1} in the IR spectra of the samples prepared by GN, SG, and CS is assigned to the IR absorption vibration of NO_3^- anions, which indicates that the NO_3^- anions in the sample precursors were not completely removed [12]. For the sample prepared by hydrothermal synthesis, a new, wide band at 3 600 cm^{-1} is present, and this is assigned to the stretching vibration of the O–H bond in $\text{La}(\text{OH})_3$ and the band at 1 500 cm^{-1} is assigned to $\text{La}(\text{CO}_3)_3$ in its segregated phase [13]. The results are in good agreement with the XRD results.

2.2 Redox properties

H_2 -TPR curves of the samples prepared by the five different methods are shown in Fig. 3. Two or more reduction peaks are present and these correspond to a multiple-step reduction of oxygen species with different reactivities. As reported in Ref. [14], the H_2 -TPR profile of the non-substituted LaMnO_3 perovskite has two reduction peaks, the first one centered at 400 $^\circ\text{C}$ and the second one at ~ 800 $^\circ\text{C}$ and these are related to the reduction of Mn^{4+} to Mn^{3+} and Mn^{3+} to Mn^{2+} , respectively.

Fig. 3. H_2 -TPR profiles of the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ catalysts prepared by different methods and calcined at 700 $^\circ\text{C}$.

In the H_2 -TPR profiles of the Mg-doped LaMnO_3 perovskites prepared by GN and SG, three reduction peaks are present. The first peak overlaps with the second peak and their highest temperatures are 358 and 464 $^\circ\text{C}$, respectively. The third peak is located at ~ 800 $^\circ\text{C}$. The low temperature peaks are attributed to the reduction of active Mn^{4+} to Mn^{3+} and also to unstable Mn^{3+} to Mn^{2+} reduction [15]. Compared with the SG sample, the GN sample has a larger peak area at 358 $^\circ\text{C}$, which is related to the more active Mn^{4+} species in the catalyst and leads to more surface oxygen species being present. Furthermore, an additional peak

appears at 260 $^\circ\text{C}$, which might originate from a Mg-substituted perovskite species with different surface properties. There is also another reason that the segregated manganese oxide (MnO_2) is reduced at this temperature and this is explained in the next paragraph [16].

The peak temperature in the H_2 -TPR profiles is related to the ability of the catalysts to bind with chemically adsorbed oxygen and lattice oxygen. The chemisorbed oxygen species and lattice oxygen species on the catalyst's surface or in its vacancies are more flexible as indicated by the peak temperature shifting to a lower temperature in the H_2 -TPR curves [17]. In the H_2 -TPR curve of the CP sample, the peak at 358 $^\circ\text{C}$ merges gradually with the peak at 464 $^\circ\text{C}$ to form a large peak at 405 $^\circ\text{C}$. However, the two original peaks do not disappear completely and this means that the reactivity of the surface oxygen species weakens. For the sample prepared by combustion synthesis, two low-temperature peaks completely overlap and form a single peak at 484 $^\circ\text{C}$ and this is attributed to the reduction of Mn^{3+} to Mn^{2+} [16,18].

2.3 Catalytic activity for methane combustion

The catalytic performance of the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ samples prepared by different methods and calcined at 700 $^\circ\text{C}$ is shown in Fig. 4. The catalytic activities of the samples decrease in the order $\text{GN} > \text{SG} > \text{CP} > \text{CS} > \text{HS}$, which is the same as the order of crystallite size for the perovskite catalysts. This shows that smaller catalyst crystallite sizes leads to higher methane combustion activity.

The effect of calcination temperature on the activities of the five catalysts used for methane combustion is listed in Table 2. T_{10} (the reaction temperature at 10% methane conversion), T_{50} , and T_{90} are used as the activity parameters for the catalysts. The results show that the preparation method and calcination temperature greatly influence the catalytic performance of $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ for methane oxidation. (1) As perovskite catalysts, the samples calcined at 700 $^\circ\text{C}$ have

Fig. 4. Catalytic activity of the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ catalysts (calcined at 700 $^\circ\text{C}$) prepared by different methods for methane combustion.

Table 2 Catalytic activities of the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ catalysts prepared by different methods and calcined at 600, 700, and 850 °C for methane combustion

Sample	Calcined at 600 °C			Calcined at 700 °C			Calcined at 850 °C		
	$T_{10}/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$	$T_{10}/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$	$T_{10}/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$
GN	445	559	653	383	444	513	430	522	635
SG	411	490	578	413	500	598	451	544	642
CP	432	533	633	435	531	624	462	573	697
CS	483	592	679	448	554	648	475	583	691
HS	516	619	707	478	596	688	504	603	687

higher catalytic activities independent of the preparation method used and, therefore, 700 °C is an appropriate calcination temperature. (2) For the five samples calcined at 700 °C and 850 °C, respectively, the effect of preparation method on the catalytic activity has the same tendency. The catalyst prepared by the glycine-nitrate method has the best catalytic performance for methane oxidation. (3) After calcination at 600 °C, the SG sample has the best activity, which is explained by the conjunct influence of the smaller crystallite size (14.4 nm) and larger surface area (25.3 m^2/g).

The results mentioned above show that although the CP sample has a larger surface area, its poor performance during methane combustion is due to the formation of precipitate particles not being uniform at the molecular level resulting in a larger crystallite size (15.1–16.7 nm). The weaker reactivity of the surface oxygen species is another reason for the lower catalytic activity. The poor catalytic activity of the HS sample is due to the existence of lanthanum oxide carbonate ($\text{La}_2\text{O}_2\text{CO}_3$, La_2CO_3) and lanthanum hydroxide $\text{La}(\text{OH})_3$ with broad XRD peaks or without a perovskite structure. In combustion synthesis, urea is not able to mix the metal ion complexes homogeneously resulting in the largest particle sizes (16.8–17.0 nm), the lowest surface area (5.1–9.9 m^2/g) and the absence of Mn^{4+} cations from the catalysts. In the sol-gel method, by complexing the precursor ions, all the reactants are well dispersed at the molecular level and no metal ions need to be removed from the starting materials, which makes the SG sample highly pure with a smaller crystallite size (13.8–15.8 nm) as well as a larger surface area (12.6–25.3 m^2/g) resulting in the presence of a large amount of active Mn^{4+} species or active surface oxygen species. These factors are responsible for its high catalytic activity.

The sample prepared by the GN method shows higher activity ($T_{10} = 383$ °C; $T_{90} = 513$ °C) than the other four samples. In fact, the GN method is a combustion process where glycine acts as a fuel and a complexing agent to complex metal cations with its carboxylic acid group at one end and an amino group at the other end. The complexation process increases the solubility of the metal ions and helps to maintain homogeneity by preventing their selective precipitation.

Therefore, single-phase perovskites are obtained. As a result, the GN samples without impurities (as Na ions in CP method) have a higher surface area (17.0–20.8 m^2/g) and the smallest crystallites (12.4–13.9 nm). Furthermore, more active Mn^{4+} species on the catalyst makes the surface oxygen species in both adsorption and chemisorbed state more flexible and reactive, resulting in high catalytic activity for methane combustion.

3 Conclusions

In summary, the highly effective $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ perovskite catalyst was successfully prepared by the glycine-nitrate method and the calcination temperature is an important factor that influences the performance of the perovskite catalyst. Among the five preparation methods used, only the hydrothermal synthesis method did not deliver a pure perovskite material. For the $\text{LaMn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ perovskite catalysts prepared by the glycine-nitrate, sol-gel, co-precipitation and combustion synthesis methods for methane combustion, we found that 700 °C is an appropriate calcination temperature and the samples calcined at 700 °C have a higher surface area and smaller crystallite size as well as a stable perovskite structure. The sample prepared by the glycine-nitrate method and calcined at 700 °C has the highest activity for methane combustion, which is due to its higher surface area, smaller crystallite size, and its low temperature redox properties, that is, there are more Mn^{4+} species on its surface to allow for flexible and reactive chemisorbed oxygen species.

References

- Porta P, De Rossi S, Faticanti M, Minelli G, Pettiti I, Lisi L, Turco M. *J Solid State Chem*, 1999, **146**: 291
- Kaddouri A, Gelin P, Dupont N. *Catal Commun*, 2009, **10**: 1085
- de la Cruz R M G, Falcon H, Pena M A, Fierro J L G. *Appl Catal B*, 2001, **33**: 45
- Saracco G, Geobaldo F, Baldi G. *Appl Catal B*, 1999, **20**: 277
- 吴跃辉, 罗来涛, 刘伟. 石油与天然气化工 (Wu Y H, Luo L T, Liu W. *Chem Eng Oil Gas*), 2007, **36**: 101

- 6 Ifrah S, Kaddouri A, Gelin P, Leonard D. *C R Chim*, 2007, **10**: 1216
- 7 Gosavi P V, Biniwale R B. *Mater Chem Phys*, 2010, **119**: 324
- 8 颜学敏, 钟润牙. 陶瓷科学与艺术 (Yan X M, Zhong R Y. *Ceram Sci Art*), 2004, (4): 39
- 9 Liu S W, Xiu Z L, Liu J A, Xu F X, Yu W N, Yu J X, Feng G J. *J Alloys Compd*, 2008, **457**: L12
- 10 翁端, 丁红梅, 吴晓东, 徐鲁华, 陈震. 物理化学学报 (Weng D, Ding H M, Wu X D, Xu L H, Chen Zh. *Acta Phys-Chim Sin*), 2001, **17**: 248
- 11 Marinho É P, Souza A G, de Melo D S, Santos I M G, Melo D M A, de Silva W J. *J Therm Anal Calorim*, 2007, **87**: 801
- 12 Bernard C, Durand B, Verelst M, Lecante P. *J Mater Sci*, 2004, **39**: 2821
- 13 Pecchi G, Campos C, Pena O. *Mater Res Bull*, 2009, **44**: 846
- 14 Lisi L, Bagnasco G, Ciambelli P, De Rossi S, Porta P, Russo G, Turco M. *J Solid State Chem*, 1999, **146**: 176
- 15 Levasseur B, Kaliaguine S. *Appl Catal A*, 2008, **343**: 29
- 16 Svensson E E, Nassos S, Boutonnet M, Järås S G. *Catal Today*, 2006, **117**: 484
- 17 刘伟, 罗来涛, 吴跃辉. 中国稀土学报 (Liu W, Luo L T, Wu Y H. *J Chin Rare Earth Soc*), 2008, **26**: 135
- 18 Cimino S, Lisi L, De Rossi S, Faticanti M, Porta P. *Appl Catal B*, 2003, **43**: 397