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A Novel Grind Process to Synthesize Nano-Micron Structured $LaMnO_3$ for Catalytic Combustion of Methane

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Abstract A novel grind route for preparing $LaMnO_3$ perovskitic catalysts for methane combustion has been developed. The method was carried out using the urea solid solution as precursors, which led to the process possessing the properties of both the liquid reaction and the low-temperature solid reaction. The resulting material exhibited nano-micron structure and possessed the high dispersion of the different components, resulting in the higher activity and the thermo-stability of the catalyst than that prepared with the conventional sol–gel-citrate (SGC) method.

Keywords Perovskite · Methane · Catalytic combustion · Nano-micron · Grind

1 Introduction

The vast majority of catalysts used in modern chemical industry are based on mixed metal oxides. The preparation of specific tailor-made mixed oxides able to perform complex functions is one of the main topics of research in the field of heterogeneous catalysis [1, 2]. In the synthesis of these materials, two factors are always considered. One is how to obtain the precursors with a uniform particle size and structure; the other is how to obtain the precursors with a homogeneous dispersion of the different components. Concerning the former, some methods, such as the microemulsion techniques, the hydrothermal method, the template [3–5], were developed; as for the latter, some methods, such as the sol–gel, the flame-spray pyrolysis, the sol–gel-citrate (SGC) [5–7], were developed. However, fulfillment of the both factors synchronous seemed to be a challenge to researchers. Zarur and Ying developed a sol–gel processing in reverse microemulsions route to prepare nanostructured complex oxides (hexaaluminate) and obtained the catalysts with ultrahigh activity and thermo-stability [8]. The route dealt with the factors smartly. However, it was costly and hard to prepare most of mixed-oxides nanoparticles for the rare reagents and the complicated synthesis process.

The perovskitic tailor-made complex oxides of formula $ABO_{3+\delta}$ are well-known as the fairly fascinating materials for its properties in catalytic, electric, magnetic, and optical areas [2, 9]. The preparation procedure is of importance to determine the properties of these materials. Various preparation methods can be found in the literature [4, 10–15], however, they all more or less suffered from the challenge mentioned above.

Here we present a novel grind synthesis of $LaMnO_3$ perovskite for catalytic combustion of methane. The key strategy is the introduction of the low temperature urea solid solutions of nitrate and KOH as precursors. The procedure possesses the properties of both the liquid reaction and the low-temperature solid reaction, and the resulting materials exhibits significant catalytic activity in methane combustion.

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2 Experimental

2.1 Catalyst Preparation

The $LaMnO_3$ catalysts were prepared by a novel grind process. In a typical synthesis, La $(NO_3)_3 \cdot 6H_2O$ (5 mmol, 2.16 g), 50 wt% Mn $(NO_3)_2$ aqueous solution (5 mmol, 1.16 mL), NH_4NO_3 (10 mmol, 0.8 g) and urea (5.0 g) were plunged into a beaker and heated in a oven at 80 °C for 20 min, then, the solid solution (a) was obtained; likewise, 82 wt% KOH (35 mmol, 2.4 g) and urea (5.0 g) were maintained in the oven at 80 °C for 20 min and formed the solid solution (b). The solution (a) and the solution (b) were transferred into a glass mortar and ground immediately. The mixed solution became viscous within 10 s, and then formed powder within 2 min. The powder was ground continuously for 10 min, then placed in air at room temperature for 12 h. Finally, the powder was washed with distilled water to remove impurities, and dried. The obtained sample was calcined at 700 or 1000 °C for 2 h. Correspondingly, the catalysts were designated as g-700 and g-1000.

For comparison, the well-established SGC method [7] was used. Briefly, the individual aqueous solutions of metal nitrates $((La/Mn)_{nominal} = 1)$ were mixed thoroughly with each other. Citric acid $((\text{citric acid}/(La + Mn))_{nominal} = 1.2)$ was added as the complexing agent to the above solution. The water in excess was evaporated by a rotatory evaporator at 70 °C. The obtained viscous gel was then dried at 100 °C. The spongy material obtained was crushed and calcined in air at 700 or 1000 °C for 2 h. The obtained catalysts were marked as s-700 and s-1000.

2.2 Catalyst Characterization

The field-emission scanning electron microscope (FE-SEM) images were taken using a JEOL JSM-6701F operated at an accelerating voltage of 5 kV.

Powder X-ray diffraction (XRD) patterns of the samples were recorded on the Shimadzu XD-3A diffractometer using Cu Kα radiation.

Specific surface areas were calculated by the BET method from the N_2 adsorption isotherms, recorded at liquid nitrogen temperature on a ASAP-2010 micromeritics apparatus. Prior to the adsorption measurements, the samples were out-gassed at 200 °C for 4 h.

2.3 Activity Tests

The reaction of methane combustion was carried out in a conventional flow system under atmospheric pressure. The catalyst (0.2 g) (20–40 mesh) and quartz powder (0.8 g, of the same particle size) were loaded in a quartz reactor (i.d. 10 mm), with quartz fiber packed at the end of the catalyst bed. Before each run, the catalyst was activated in flowing air (100 $cm^3\ min^{-1}$) with the temperature increased at a rate of 10 °C min^{-1} to 600 °C, where it was maintained for 0.5 h. After cooling in the flowing air down to 350 °C, the activity tests were carried out by feeding 100 $cm^3\ min^{-1}$ of a mixture gas of 1 vol% CH_4 (air as the balance). The inlet and outlet gas compositions were analyzed by an on-line gas chromatograph with a packed column of carbon molecular sieve and a thermal conductivity detector.

3 Results and Discussion

The process was carried out based on low-temperature solid solution of the urea. The melt point of the urea declines by the dissolution of the salt in it. In the experiment, the nitrate urea solution in a suitable ratio retained liquid state under 0 °C. Similarly, the KOH urea solution could be obtained above 70 °C. When the two urea solutions were mixed together, the reaction occurred by two steps marked in Fig. 1 From point (A) to point (B), the molar ratio of salt to urea decreased owing to the formation of the precipitate. Consequently, a new (L + S) state was formed, i.e., the particles of precipitate and frozen urea were filled with the unset solution. From point (B) to point (C), as the temperature declined, the unset solution froze.

The two-step reaction induced to form a special morphology. In the first step, the formation of the precipitate was accompanied by the urea crystal, which prevented the excess growth of the precipitate; meanwhile, the formed urea crystal played an important role like a template. In the

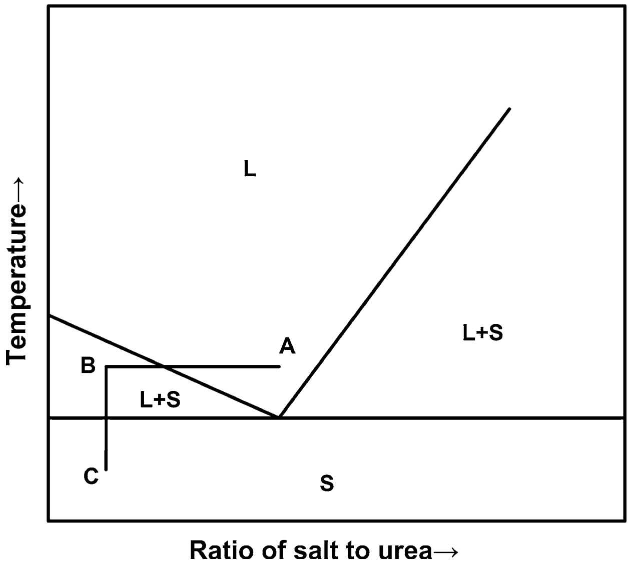

Fig. 1 A simple binary phase diagram of salt and urea (L: liquid; S: solid; points A, B, and C correspond to the three states of the reaction)

second step, massive urea crystal was formed with the decline of the temperature, in which the precipitate grew into a reticulation with the same morphology owing to the bonding of hydroxyl. The morphology of g-700 is presented in Fig. 2a–c. The catalyst is mainly composed of spherical particles of 25–35 nm in diameter. Furthermore, the linked particles form a flake-like spongy material of 2–5 μm in size as the secondary structure. It's inferred that the grind process was responsible for the formation of the flake structure. For comparison, the morphology of s-700 is presented in Fig. 2d, it can be observed that the material was composed of the disorder and irregular particles, suggesting the poorer thermal-stability of the material as compared to g-700. Moreover, the specical nano-micron structure of the material synthesized by the grind process can display lots of potential properties. It possesses the properties of the usual nano-material, such as favorable to mass transfer, more defects as active sites, at the same time, the materials with the micro-structure are easy to separate from solution, which is usually a problem in the nano-materials synthesis. The simple process of preparation and separation will promote the industrial applications.

Moreover, the solid solution instead of salt used as precursors makes the procedure possess the properties of liquid reaction and low-temperature solid reaction. The liquid reaction has the properties of high dispersion of different metal ions and quick reaction. Obviously, the quick reaction is favorable to reduce the negative influence of diffusion. It is worth noting that ammonium nitrate added to the solution has two functions. Firstly, it plays the role of buffer solution and stabilizes the pH value of the solution; secondly, the diffusion of NH_3 produced by the reaction of the ammonium nitrate and the KOH can promote the quick reaction. After the reaction, the liquid state was transformed immediately to the solid state, leading to the procedure exhibitted the properties of the low-temperature solid reaction, including regular structure and hindering the effect of recrystallization. Then the sample was placed in air at room temperature, in which the Mn(II) ions could be oxidized to the higher valency effectively, and the precipitate grew slowly to form the secondary structure. All these factors facilitate to form the excellent precusor with high dispersion of the different components, which is always a challenge to the conventional grind method [15].

The XRD patterns of the catalysts are shown in Fig. 3. The single perovskite phase (JCPDS Number: 75-0440) is formed in every catalyst. However, it can be concluded from the diffraction pattern that the sintering degree of the catalysts synthesized with the grind route from 700 to 1000 °C is slighter than that of the catalyst prepared with the SGC method, consistent with the morphology described above. Moreover, it is supported by the surface information summarized in Table. 1. The surface, pore volume and pore size of the catalysts synthesized by the grind process are suprior to those of the catalysts prepared by the SGC

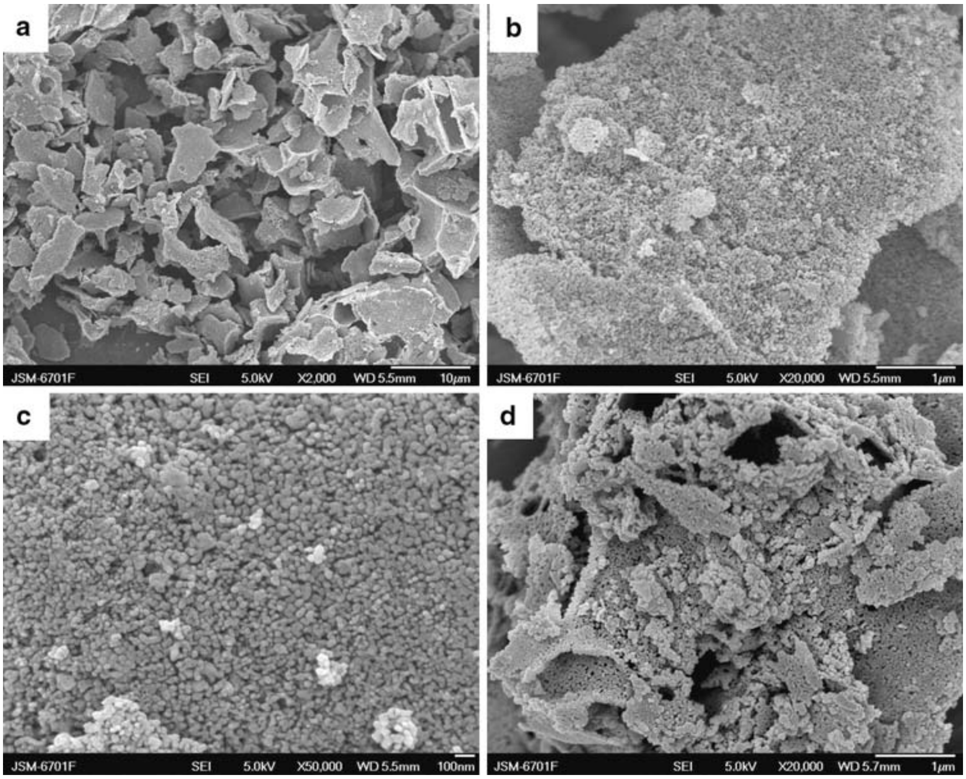

Fig. 2 FE-SEM of the catalysts: **a**, **b**, and **c** are the images of g-700; **d** is the image of the s-700

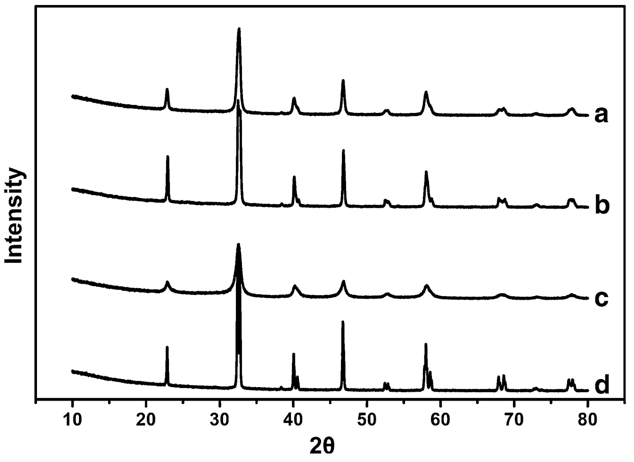

Fig. 3 XRD patterns of the catalysts: **a** g-700, **b** g-1000, **c** s-700, and **d** s-1000

Table 1 Surface area and pore structure

Catalysts	S_{BET} (m^2 g^{-1})	V_{pore} (cm^3 g^{-1}, BJH)	D_{pore} (nm, BJH)
g-700	27.7	0.19	27.0
g-1000	4.9	0.014	11.4
s-700	26.7	0.12	16.3
s-1000	3.7	0.008	8.5

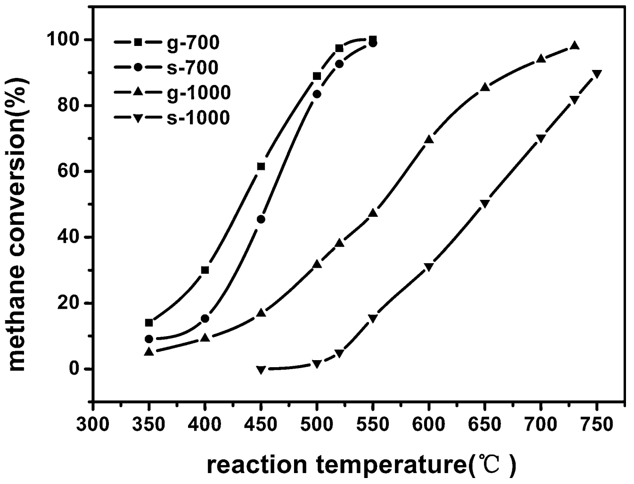

Fig. 4 Light-off curves of methane conversion over the LaMnO$_3$ perovskites prepared by the grind route and the SGC method

method. Especially, the surface area of the catalyst calcined at 1000 °C was considerablely enhanced (g-1000: 4.9 m^2 g^{-1}, s-1000: 3.7 m^2 g^{-1}) because the perovskite is a kind of material inclined to sinter and agglomeration.

The catalytic activities in methane combustion over the catalysts are shown in Fig. 4. It can be observed that the catalysts prepared with the grind process exhibit significantly higher activity than those prepared with SGC method at the same calcination temperature. It is inferred that the excellent activity is ascribed to the two factors described above.

4 Conclusions

A novel grind route for preparing the LaMnO$_3$ perovskites was developed. The procedure exhibited the properties of both the liquid reaction and the low-temperature solid reaction. The resulting materials showed the significantly catalytic activity in methane combustion.

Moreover, the method can be employed to synthesize nano-micron materials economically, especially, to synthesize multi-component catalysts based on the excellent solubility of the acidic or alkaline compounds in the urea.

References

1. Tejuca LG, Fierro JLG, Tascón JMD (1989) Adv Catal 36:237
2. Peña MA, Fierro JLG (1981) Chem Rev 101:2001
3. Eriksson S, Nylén U, Rojas S, Boutonnet M (2004) Appl Catal A 265:207
4. Valdés-Solís T, Marbán G, Fuertes AB (1919) Chem Mater 17:2005
5. Cushing BL, Kolesnichenko VL, O'Connor CJ (2004) Chem Rev 104:3893
6. Kammler HK, Madler L, Pratsinis SE (2001) Chem Eng Technol 24:583
7. Baythoun MSG, Sale FR (2757) J Mater Sci 17:1982
8. Zarur AJ, Ying JY (2000) Nature 403:65
9. Seiyama T (1992) Catal Rev 34:281
10. Delmon BJ (2007) Therm Anal Calorim 90:49
11. Hu CG, Liu H, Lao CS, Zhang LY, Davidovic D, Wang ZL (2006) J Phys Chem B 110:14050
12. Vázquez-Vázquez C, López-Quintela MA (2006) J Solid State Chem 179:3229
13. Chiarello GL, Rossetti I, Forni L (2005) J Catal 236:251
14. Pecchi G, Reyes P, Zamora R, Campos C, Cadús LE, Barbero BP (2008) Catal Today 420:133–135
15. Ito T, Zhang QW, Saito F (2004) Powder Technol 170:143–144