

Synthesis of nanoparticle Ce–Mg–O mixed oxide as efficient support for methane oxidation

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Abstract

A new material of Ce–Mg–O nanoparticle, which can be applied as catalyst support for methane combustion reaction, has been successfully synthesized and characterized by XRD, AFM and temperature-programmed reduction (TPR). It was found that the activity of methane combustion over Ce–Mg–O as a catalyst support is optimistic (the methane conversion reaches 90% at 560 °C over FeO/Ce_{0.1}Mg_{0.9}O_{1.1} catalyst). The design of adding alkaline-earth metals into CeO₂, the typical structure of Mg²⁺ enters the lattice of CeO₂ to form a solid solution, whose activity for methane combustion is reasonable. The effect of nanoparticle and good redox ability of Ce–Mg–O are also key factors affecting catalyst activity.

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1. Introduction

The production of energy by the combustion of methane or natural gas has recently attracted growing interest. Catalytic combustion of methane is a widely applied in energy supply using natural gas for industrial as well as domestic applications [1,2]. Otherwise, catalytic combustion of methane is one of the most effective methods to significantly reduce pollutants (HC, CO and NO_x) [3]. Among the catalysts for methane combustion, the supported noble metals (Pt and Pd) have been generally used [4,5]. However, supported noble metals, although very active, are not fully satisfactory, due to their high price and scarce resource. Various transition metal oxides have been investigated as catalysts for catalytic combustion of methane but they are less active than noble metals [6–8]. The aforementioned reasons led us to begin a study to find a new type of catalyst for methane combustion. Ceria (CeO₂) has been widely used as a promoter and an oxidation catalyst because of its unique redox properties and high oxygen storage capacity [9,10]. Nowadays, the rapid growth in

the applications and the characterization of CeO₂-containing catalysts has been well documented [11,12].

Studies of new material with nanoparticles have attracted much attention in recently years. When material is small enough, in nanometer size, it shows many typical properties of high surface area and high activation energy, for using it as support in catalyst [13,14]. The catalytic activity of the supported catalyst system is affected by the size of the support particles. The size effect in Au catalyzed CO oxidation shows an outstanding fraction in catalysis [15]. Thus, the nanoparticles preparation technology can improve the efficiency of catalyst in its catalytic activity.

In our previous work, we have also reported that the synthesized Ce–Zr–Ba nanoparticles powders show excellent results in surface area, high heat resistance and catalytic activity for CO oxidation [16]. At the present, there are some views with regard to the size effect of nanoparticle in supported catalysis. But mainly focus on the study of metal nanostructured materials as active compound [17]. There are little reporters about synthesis of nanoparticles material as support to improving catalytic activity. In order to develop the new application of the nanoparticle material, to design a new material used as catalyst support to improve the methane oxidation

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activity was appears to be obvious in this study. In the present paper, we have investigated the Ce–Mg–O new material as a support on the methane oxidation reaction. The morphology of Ce–Mg–O new material was demonstrated by AFM, the structural character was investigated by XRD. As well as the redox capability of Ce–Mg–O was also studied by TPR technique.

2. Experimental

2.1. Catalyst preparation

New nanoparticles Ce–Mg–O material was prepared by macromolecule surfactant modified method. It described as following: the mixing solutions of $\text{Ce}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ were, respectively, by a given amount, which was dependent on the designed composition of the mixed oxide. Then, on a certain churn up rate, the mixed solutions were added into a 5 wt% polyethylene glycol-20,000 the resultant mixture was stirred at room temperature using a magnetic agitator. The gel was put into the refrigerator at the temperature of below 0°C for 24 h, then adding *n*-butyl alcohol to azeotropic distillation with the precursors in order to dry the water both of surface and interstitial position of the sample. After washing many times, the sample was dried at 120°C overnight and then calained at 650°C for 4 h in air atmosphere.

2.2. Catalytic activity measurement

The test of methane combustion was carried out in a fixed-bed reactor by using 150 mg of sample. The reaction gases for methane combustion consisted of 2.5% CH_4 and 6.0% O_2 in N_2 . The flow rate of the feed gas was 80 ml min^{-1} . The analysis of the effluent from the reactor was performed by a SP-2304 model gas chromatograph with a thermal conductor (TCD). The reaction was kept at each temperature for about 0.5 h to achieve steady activity.

2.3. Characterization

Thermo-gravimetric analyses (TG) were carried out on a PE TGA 7 instruction at a heating rate of $20^\circ\text{C min}^{-1}$ from 50 to 800°C on 10 mg of sample. Atom force microscope (AFM) photographs were carried on SPA-200 instrument. X-ray power diffraction (XRD) power patterns were collected on a Rigaku D/max-III B instrument using $\text{Cu K}\alpha$ radiation (40 kV and 40 mA). Diffraction peaks recorded between 20° and 80° has been used to identify the structure obtained.

2.4. Temperature-programmed reduction (TPR) measurement

TPR was carried out in an instrument typed AMI-200 equipped with a TCD detector. The sample (100 mg) was

fixed in a quartz reactor by packing quartz wool at both ends and pretreated in He flow at 400°C for 1 h to remove the adsorbed carbonates and hydrates. After cooling down to room temperature (25°C) and introducing the reduction gas of 5% H_2/Ar , the sample was heated at a rate of $20^\circ\text{C min}^{-1}$ from room temperature to 800°C . After the first TPR was recorded, the sample was further subjected to re-oxidation with 20% O_2/N_2 at 100°C for 30 min, after cooling in O_2 to room temperature, the feed gas was switched to a He stream (50 ml min^{-1}) for TPD. Subsequently, after the first TPD measurement, the sample was re-activated in an O_2 stream at 300°C for 0.5 h, then to record second TPD. In every case, no reaction products except carbon dioxide and water were detected.

3. Result and discussion

3.1. Catalytic activity test

As shown in Table 1, the data indicated that the behavior of methane combustion in prepared Ce–Mg–O new material was excellent. The methane oxidation activities of bulk CeO_2 and MgO were quite low; the T_{10} (temperature for 10% conversion of methane), T_{50} and T_{90} of bulk CeO_2 are, respectively, at 690, 730 and 820°C . And bulk MgO showd less activity in methane combustion similarly. But the activities of series of Ce–Mg–O samples were much higher than CeO_2 and MgO . As indicated in Table 1, $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_{1.8}$ sample had a methane conversion temperature of 680°C at T_{90} and in $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{O}_{1.1}$ sample the temperature of 630°C at T_{90} , suggesting that the catalytic activities enhanced with the increasing of MgO ratio. The sequence of catalytic activities in Ce/Mg ratio was $\text{Ce/Mg} = 1/9 > \text{Ce/Mg} = 1/1 > \text{Ce/Mg} = 9/1$. We assume that addition of Mg leads a significant increase in methane oxidation activity. Table 1 also showed catalytic activity of $\text{FeO/Ce}_{0.1}\text{Mg}_{0.9}\text{O}_{1.1}$ catalyst for methane oxidation with various FeO contents. The catalytic activity enhanced with the increasing of the content of FeO,

Table 1
Activity of Ce–Mg–O, $\text{FeO/Ce}_{0.1}\text{Mg}_{0.9}\text{O}_{1.1}$ and $\text{PdO/Ce}_{0.1}\text{Mg}_{0.9}\text{O}_x$ catalysts for methane combustion

Sample	T_{10} ($^\circ\text{C}$)	T_{50} ($^\circ\text{C}$)	T_{90} ($^\circ\text{C}$)
CeO_2	690	730	820
MgO	700	760	790
$\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_{1.8}$	520	620	680
$\text{Ce}_{0.5}\text{Mg}_{0.5}\text{O}_{1.5}$	510	600	660
$\text{Ce}_{0.1}\text{Mg}_{0.9}\text{O}_{1.1}$	500	570	630
1.0% FeO/CeO_2	680	700	750
5.0% FeO/CeO_2	660	670	740
7.0% FeO/CeO_2	620	660	700
1.0% $\text{FeO/Ce}_{0.1}\text{Mg}_{0.9}\text{O}_{1.1}$	480	560	600
5.0% $\text{FeO/Ce}_{0.1}\text{Mg}_{0.9}\text{O}_{1.1}$	440	520	590
7.0% $\text{FeO/Ce}_{0.1}\text{Mg}_{0.9}\text{O}_{1.1}$	390	490	560
10.0% $\text{FeO/Ce}_{0.1}\text{Mg}_{0.9}\text{O}_{1.1}$	410	510	580
1.0% $\text{PdO/Ce}_{0.1}\text{Mg}_{0.9}\text{O}_{1.1}$	410	480	570

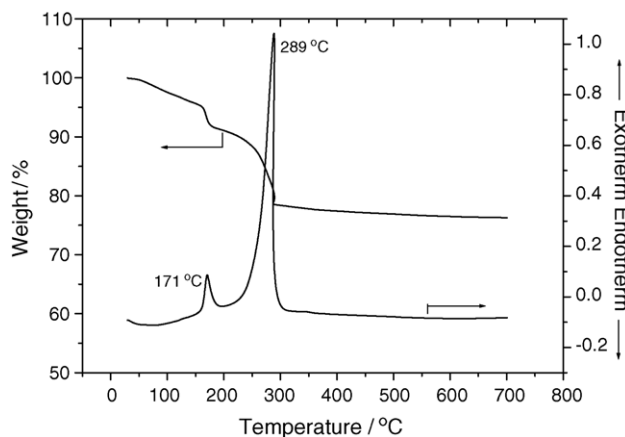


Fig. 1. TG-DTA curve of Ce-Mg-O sample.

but when the content of FeO was higher than 7.0%, the catalytic activity decreased. This indicated that the optimal fraction of FeO in catalyst was 7.0%. The activity decrease may be due to excessive FeO enrichment of the catalyst surface. Moreover, the activities of FeO/Ce-Mg-O and FeO/CeO₂ were also compared, and the former catalyst was found to be more active obviously. The temperature for 90% conversion of methane was decreased from 700 to 560 °C by replacing Ce-Mg-O with CeO₂ as catalyst support. In addition, it should be pointed out that FeO/Ce_{0.1}Mg_{0.9}O_{1.1} catalyst could be obtained the same catalytic activity as the PdO/Ce_{0.1}Mg_{0.9}O_{1.1} catalysts at low temperature, respectively. On the basis of the activity results, we propose that Ce-Mg-O was an active support for methane oxidation, in which shows drastic changes compared with bulk CeO₂ or MgO.

3.2. TG-DTA result

Fig. 1 showed the TG-DTA curves of Ce-Mg-O sample. The DTA curve revealed that there were two exothermic peaks at temperature of 171 and 289 °C and corresponding there were two weight loss in the temperature range of 170–300 °C in TG curve. The two peaks could be attributing to the thermal decomposition of organic substance in the sample. There was no endothermic peak at nearly 100–120 °C. This result was very important because it shows that Ce-Mg-O new material can be prepared by the typical method of dry the water effectively both in the surface and interstitial position. The preparation method might be due to the formation of agglomeration-free nanoparticles and favoring the catalytic activity.

3.3. Structural characters and the morphologies analysis

To elucidate the effects of Ce-Mg-O new material as catalyst support, the microstructure and three-dimensional shape in particle size of Ce-Mg-O were examined by AFM.

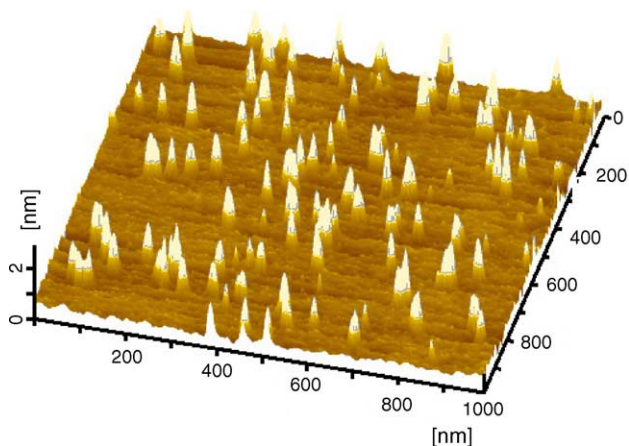


Fig. 2. AFM diagram of Ce-Mg-O sample.

The average value of the crystallite size of the synthesized Ce-Mg-O new material was within 30–40 nm (shown in Fig. 2) and the distribution state of the sample can be seen clearly. The particles showed an equality distribution without agglomeration. Statistical analysis of diameter and height for one particle size of Ce-Mg-O from the AFM section analysis were reported in Fig. 3. As shown in Fig. 3, every Ce-Mg-O nanoparticles with sizes about 30–50 nm and height at about 0.87 nm was detected. At this image, essentially each particle showed by a smooth surface. It seems that the nature of suitable structure and the particle size of Ce-Mg-O new material could be regarded to play key roles in methane combustion reaction.

Fig. 4 showed the XRD patterns of CeO₂, MgO and Ce-Mg-O new material with different Ce/Mg ratio. It can be seen clearly that the characteristic peak of fluorite type of CeO₂ can be detected on each Ce-Mg-O sample, which was located, respectively, on 28.57°, 33.85°, 47.53° and 56.39° in 2θ. There were no visible peaks due to crystal lines about magnesium phase or any other oxide compounds. The typical CeO₂ characteristic peak appeared shift to higher angles with the increase of magnesium ratio in Ce-Mg-O series samples, suggesting insertion of smaller Mg²⁺ ions in the lattice of CeO₂ to form a solid solution and maintaining the cubic-fluorite structure. It was previously found [18] that the fluorite-structure mixed oxide catalysts is favorable to methane combustion. In our study, as can be seen in Table 1 and Fig. 4, the results were correlated well with the opinion. Moreover, the variation in lattice parameters for these Ce-Mg-O samples at different Ce/Mg ratios is shown in Table 2. As addition of Mg²⁺ into CeO₂, the cell parameters get reduced, indicates Mg²⁺ enters the cube lattice of CeO₂

Table 2
Lattice parameter of Ce-Mg-O samples with Mg/Ce ratio

Sample	Mg/Ce = 1/9	Mg/Ce = 1/1	Mg/Ce = 9/1
<i>d</i> (nm)	0.5425	0.5411	0.5409
Cell type	Cubic (F-center)	Cubic (F-center)	Cubic (F-center)

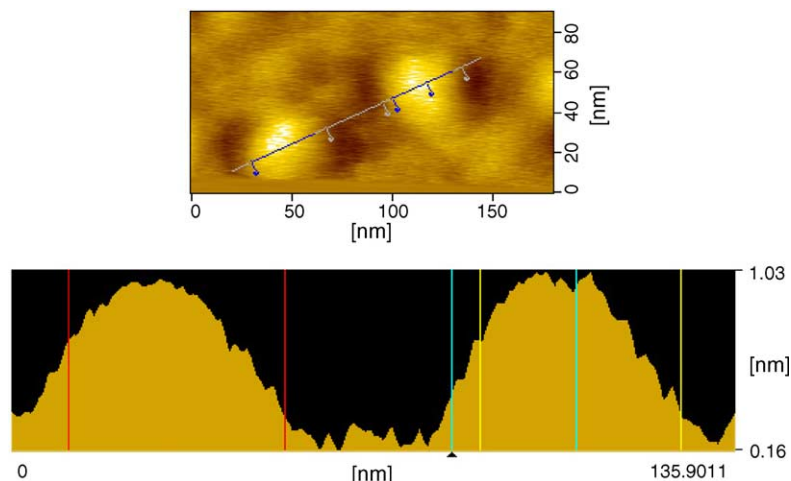


Fig. 3. AFM diagram of Ce–Mg–O sample in particle size.

and arose partly changes in CeO₂ structure. The values of lattice parameters for Ce–Mg–O samples were 0.5425, 0.5411 and 0.5409, respectively. This variation was due to the fact that the ion radius of Mg (0.72 Å) was smaller than the ion radius of Ce (0.87 Å), Mg can enter the CeO₂ lattice, resulting in a decrease in lattice parameter. Combining the XRD and AFM results, it was clear that the Ce–Mg–O material, with typical structure of solid solution and the nanoparticles, was favor to the catalyst support for methane combustion. Besides, the typical XRD lines of ceria became more intense with the increase of magnesium ratio, this indicated that the higher ratio of magnesium, the better the structure of the Ce–Mg–O solid solution was. Also the stronger the interaction between magnesium and ceria, the higher the catalytic activity was.

According to above results, we try to explain the effect of Ce–Mg–O support: Ce–Mg–O new material, formed by alkaline-earth metals elements introduced into the CeO₂ lat-

tice, can effectively enhance the activity of methane oxidation because it was appeared an aberration of crystal lattice of Mg²⁺ enters the cube lattice of CeO₂, thus typical structure can easily supply active oxygen vacancy and enhance the Ce⁴⁺–Ce³⁺ redox cycle.

3.4. Oxygen property

To study the reduction ability of Ce–Mg–O new material, we compare the H₂-TPR profiles of Fig. 5a and b. There are two peaks appeared at 470 and 600 °C in bulk CeO₂ sample in Fig. 5a, the reduction peak shift to 440 and 530 °C lower temperature apparently in Ce–Mg–O sample (Fig. 5b), indicating the combination of CeO₂ and MgO favors the reduction ability of CeO₂. In order to investigate the reversible redox ability of Ce–Mg–O sample, preliminary TPR process was treated by further re-oxidized at 100 and 300 °C. As indicated in Fig. 5c, the reduction temperature and relative intensities of the peaks in Ce–Mg–O sample were changed a lot after first 100 °C re-oxidation treatments. The major reduction peak of CeO₂ shift to 340 °C and another small peak appeared at 520 °C, for the second re-oxygen treatment, the TPR profiles

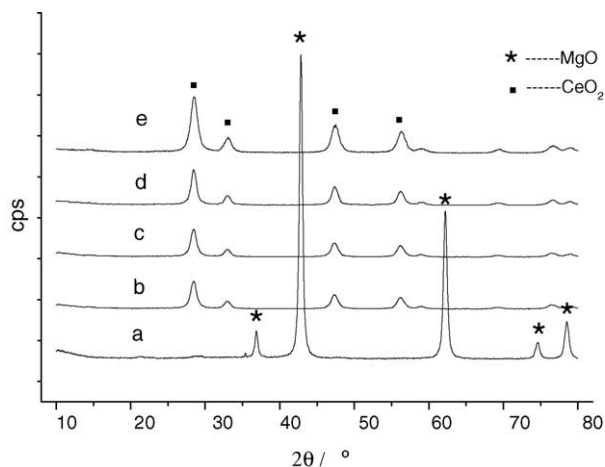


Fig. 4. XRD patterns of Ce–Mg–O samples with different Mg/Ce ratios: (a) MgO, (b) CeO₂, (c) Ce_{0.9}Mg_{0.1}O_{1.1}, (d) Ce_{0.5}Mg_{0.5}O_{1.5} and (e) Ce_{0.1}Mg_{0.9}O_{1.1}.

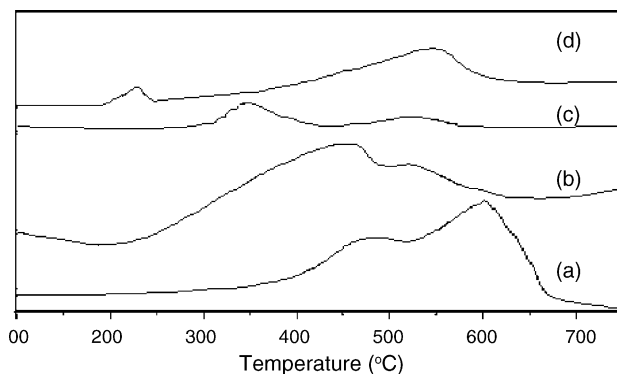


Fig. 5. TPR profiles of CeO₂ and Ce–Mg–O samples: (a) CeO₂, (b) Ce_{0.1}Mg_{0.9}O_{1.1}, (c) Ce_{0.1}Mg_{0.9}O_{1.1} re-oxidation at 100 °C and (d) Ce_{0.1}Mg_{0.9}O_{1.1} re-oxidation at 300 °C.

of the sample was also greatly changed, in which two peaks located at 225 and 550 °C were observed in Fig. 5d. It clearly indicates that reduction/oxidation processes had taken place in Ce–Mg–O new material. Thus, Ce–Mg–O new materials used as catalyst support in the methane combustion reaction can be easily re-oxidized and easily supply active oxygen species in character. As indicated in Fig. 5, Ce–Mg–O sample showed a good redox cycle, is in accordance with the Mars and Van-Krevelen (redox) mechanism and plays a role in methane combustion [19,20]. This result also adds to the understanding of the high catalytic activity in Ce–Mg–O new material used as catalyst support.

4. Conclusion

A typical catalyst support, Ce–Mg–O new material, for methane combustion is successfully synthesized by macro-molecule surfactant modified method and characterized by XRD, AFM and TPR. XRD demonstrated that Mg^{2+} enters the cube lattice of CeO_2 to form a solid solution of Ce–Mg–O, this typical structure is favorable to enhance the catalytic activity. A good distribution state of nanometer particles in Ce–Mg–O material is found by AFM. The nanometer sizes effect of Ce–Mg–O material is important to the activity of catalyst. The redox ability of Ce–Mg–O material affects the catalytic activity evidently. Moreover, the preparation process is technically simpler in its character.

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