Effect of Ni Doping on Ce–Mg–O Nanosize Catalysts for CO Oxidation

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Material of CeMg mixed oxide nanoparticle doping with Ni metal can be applied as catalyst for CO oxidation reaction. It was successfully synthesized by macromolecule surfactant modified method and characterized by XRD, BET, and TEM-EDX techniques. Both alkaline-earth (Mg^{2+}) and transition metal (Ni^{2+}) doped into CeO_2 entered the lattice of CeO_2 to form a solid solution of CeMgO and CeMgNiO, respectively. Ni doping on CeMg mixed oxide showed much better activity of CO oxidation compared to CeMg mixed oxide itself.

Introduction

Carbon monoxide (CO) is one of green house gases, mostly contributed from vehicle exhaust. CO can maintain in the troposphere about 3 years; therefore many researches make more effort to reduce its concentration. CO oxidation and selective oxidation are promising solution to reduce the concentration before emission. The supported noble metals (Au, Pt, Pd and Ir) have been widely used for CO oxidation (Ma *et al.*, 2007; Zhu *et al.*, 2007). However, supported noble metals, although very active, are not fully satisfactory, due to their high price and scarce resource. In the past few years, a great deal of attentions has been focused on cerium-based materials for used in automotive exhaust catalysts in order to reduce CO concentration (Kasaepar *et al.*, 1999; Boaro *et al.*, 2003). Ceria (CeO_2) has been widely used as a promoter and an oxidation catalyst because of its unique redox properties and high oxygen storage capacity (Costa *et al.*, 2003). To gain more effective activity, catalyst structure requires being in nanoparticles (Chen *et al.*, 2005a).

Additions of dopants (such as Zr, Ti, Mg, etc.) into Ce have been gained attention for oxidation processes (Terrbile *et al.*, 1998; Zhang *et al.*, 2006; Li *et al.*, 2007; Romero-Sarria *et al.*, 2008). They induced catalysts highly uniform nanosize particles, improving its stability and activity. The activity of catalyst was found

to be dependent on the Ce/dopant ratio. For example, $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ exhibited the highest activity in CO oxidation (Over and Muhler, 2003). As well, Ce–Mg–O new material showed excellent work in methane combustion. The activities of series of Ce–Mg–O samples were much higher than CeO_2 and MgO. $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_{1.8}$ sample showed 90% methane conversion at 680°C while 630°C for $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{O}_{1.1}$ (Chen *et al.*, 2005b).

More chemical species, such as Ba, Zn, Sn, Ni, were added into CeZr mixed oxides (Chen *et al.*, 2005a; Gridanurak *et al.*, 2007). Doping resulted in particle nanosize of 10–20 nm in diameter. $\text{CeZrSn}_{0.5}$ showed the best performance on CO oxidation with a light-off temperature region of $175\text{--}210^\circ\text{C}$. On the other hand, NiO enhanced the activity of partial oxidation of methane, when it was mixed into $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ powder. Approximately, 60% conversion of methane was observed at 700°C with good H_2/CO ratio (Chen *et al.*, 2005b).

The aim of this work was to study the influence of small addition of Ni metal to CeMg mixed oxide for CO oxidation reaction. The nanoparticle of catalyst was synthesized by macromolecule surfactant modified method in order to obtain high surface area catalyst. Furthermore, characterizations and catalytic activities on CO oxidation were also included.

1. Experimental

1.1 Catalyst preparation

Nanoparticles of CeMgO and CeMgNiO were prepared by macromolecule surfactant modified method. A solution of $\text{Ce}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ and

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Fig. 1 TEM images of CeMgO and CeMgNiO samples with different Ce/Mg ratios: (a) $\text{Ce}_{0.9}\text{Mg}_{0.1}\text{O}_2$, (b) $\text{Ce}_{0.5}\text{Mg}_{0.5}\text{O}_2$, (c) $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{O}_2$, (d) $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{-NiO}$, and EDX image of (e) $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{O}_2$ and (f) $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{-NiO}$

$\text{Ni}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ was, respectively, mixed by a given amount, which was dependent on the designed composition of the mixed oxide. The mixed solution was added with a 5 wt% polyethylene glycol–20,000 following with stirring at room temperature. Then, solution pH was adjusted to 9 by NH_4OH solution. The gel was placed below 0°C overnight, then, filtrated and added with *n*-butyl alcohol to azeotropic distillation with the precursors. After washing, the sample was calcined at 650°C for 4 h in air.

1.2 Catalyst characterization

The structure of mixed oxides was examined by X-ray diffraction (XRD), a D/max-IIIB (Rigaku Corp.), using $\text{Cu K}\alpha$ radiation and a power of $40\text{ kV} \times 40\text{ mA}$. Diffraction peaks were recorded at the 2θ between 20° –

80° . The BET surface area of each catalyst was determined by means of physisorption, using a quantachrome NOVA automated gas sorption instrument. Prior to the analysis, the samples were outgassed at 350°C for 6 h. The morphology of the samples was investigated by a transmission electron microscope–energy dispersion analysis X-ray (TEM–EDX), using a JEM-2010 (JEOL Ltd.) in which lanthanum hexaboride (LaB_6) was used as a filament.

1.3 Catalyst activity measurement

Catalytic oxidation of CO on mixed oxide catalysts was carried out in a fixed bed reactor mounted in the constant temperature ($\pm 1^\circ\text{C}$) zone of an electric furnace. A mixed oxide sample of 100 mg was packed between two

Fig. 2 XRD patterns of CeMgO and CeMgNiO samples with different Ce/Mg ratios: (a) CeO₂, (b) Ce_{0.9}Mg_{0.1}O₂, (c) Ce_{0.5}Mg_{0.5}O₂, (d) Ce_{0.1}Mg_{0.9}O₂ and (e) Ce_{0.1}Mg_{0.9}-NiO

layers of quartz wool inside a quartz tube (i.d. = 6 mm) at atmospheric pressure. Small diameter thermocouple was located in the catalyst bed. The reaction temperature ranged from 120–380°C with a total feed gas flow rate of 50 mL/min, corresponding to a gas hourly space velocity (GHSV) of 30,000 h⁻¹. The analysis of the effluents from the reactor was performed on line by a GC-8A (Shimadzu Corp.) equipped with Unibead C packing columns and a TCD detector.

2. Results and Discussion

2.1 Structural characters and the morphology analysis

To elucidate the effects of CeMgNi mixed oxide new material as a catalyst, the microstructure and three-dimensional shape in particle size of CeMgO were examined by TEM. The average value of the crystallite size of the synthesized CeMgO new material was around 11–18 nm, as shown in **Figures 1(a)–(c)**. A doping of Ni onto CeMg mixed oxides (**Figure 1(d)**) does not affect its particle size and distribution significantly, compared to CeMgO itself (**Figure 1(c)**). The particles showed an equality distribution without agglomeration both before and after adding Ni metal into the mixed oxide catalyst. In this image, essentially each particle showed a smooth surface. The EDX chemical analysis, in **Figures 1(e)–(f)**, clearly confirms the presence of Ce, Mg and Ni on studied catalysts.

Figure 2 shows the XRD patterns of CeO₂, CeMgO and CeMgNiO materials with different Ce/Mg ratio. It can be seen clearly that the characteristic peaks of fluorite type of CeO₂ can be detected on each CeMgO sample, which was located, respectively, on 28.56, 33.14, 47.5 and 56.36° in 2θ. There were no peaks due to crystal lines for magnesium phase or any other oxide compounds as also presented elsewhere (Chen *et al.*, 2005b; Shan *et*

Table 1 BET surface areas of CeMgO with different Ce/Mg ratios and CeMgNiO

Catalysts	BET surface area [m ² /g]
CeO ₂	43.72
Ce _{0.9} Mg _{0.1} O ₂	47.55
Ce _{0.5} Mg _{0.5} O ₂	55.87
Ce _{0.1} Mg _{0.9} O ₂	78.24
Ce _{0.1} Mg _{0.9} -NiO	25.21

Fig. 3 CO oxidation activity over CeMgM mixed oxides catalysts; (○) CeO₂, (▲) Ce_{0.9}Mg_{0.1}O₂, (■) Ce_{0.5}Mg_{0.5}O₂, (△) Ce_{0.1}Mg_{0.9}O₂, (◇) Ce_{0.1}Mg_{0.9}-NiO, and (●) CeNiO (solid lines: run-up; dash lines: run-down)

al., 2006). The generated fluorite type of CeO₂ suggested that insertion of Mg²⁺ in the lattice of CeO₂ could form a solid solution and maintain the cubic-fluorite structure. It was also found periclase structure of solid solution of NiO–MgO, located on 44.5, 62.7° in 2θ (Daza *et al.*, 2008).

Apart from the homogeneity of the macromolecule surfactant modified method also possesses high surface area. The BET surface area of mixed oxide catalysts are summarized in **Table 1**. The results suggested that the stability of the surface areas of the catalysts increased with increasing the content of magnesium. It was found that the surface areas of the mixed oxides were higher than the surface area of pure ceria. This might be due to the fact that the crystallite growth process was retarded or disfavored by the incorporation of magnesium ions into the CeO₂ matrix enhancing the thermal stability of the mixed oxide catalysts.

However, with doping nickel ion, the surface area of oxide sample was found to be decreased drastically. This might be caused by the migration of Ni species which can be dissolved into Ce–Mg–O like solid solution, as

confirmed by XRD pattern.

2.2 Catalytic activities of CO oxidation

The study was focused on the oxidation of CO over the mixed oxide catalysts: CeO₂, CeMg mixed oxide (Ce/Mg ratio: 1/9, 5/5 and 9/1), Ce_{0.1}Mg_{0.9}-NiO and CeNiO, as shown in **Figure 3**. It demonstrates light-off curves of CO oxidation activity for all catalysts. The catalytic activity of mixed oxide catalysts increased with increasing reaction temperature for all samples. The CO oxidation activities of all ratios of Ce/Mg were quite similar to that of T₈₀ (temperature for 80% conversion) of Ce/Mg ratio of 1/9, 5/5 and 9/1 were at 350, 370 and 350°C, respectively and were much higher than that of CeO₂ (T₈₀ was 250°C). Considering only Mg on CeO₂, it should be pointed out that an addition of Mg had no influence on CO oxidation.

Considering the catalytic activity based on T₈₀ of Ce_{0.1}Mg_{0.9}-NiO, CeNiO, and CeO₂, it was found to be 170, 207, and 244°C, respectively. The best activity of CO oxidation was performed under catalyst obtained by the coprecipitation of Ni²⁺, Mg²⁺ and Ce²⁺. As a result, addition of nickel and magnesium into Ce mixed oxide was beneficial for higher reducibility of catalyst (Daza *et al.*, 2008).

Combined with XRD and BET results, the typical structure in Ce_{0.1}Mg_{0.9}-NiO contains the active sites for low temperature CO oxidation and the catalytic activity has no direct correlation with surface areas, which was similar to results presented by Thammachart *et al.* (2001).

Conclusion

CeMg mixed oxide nanomaterial and doping with Ni metal was obtained by a macromolecule surfactant modified method. The catalysts were characterized for their crystalline structure, particle sizes, and surface area. The synthesis method resulted in the formation of solid solution of cubic fluorite, and periclase crystalline phase, moderate surface area and particle size smaller than 20 nm. Ce_{0.1}Mg_{0.9}-NiO solid solution was reported to have the highest activity among mixed oxide catalysts. It was probably reasonable that the high reducibility was more effective in CO oxidation activity than the high surface area of catalysts.

Acknowledgments

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