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Catalysis Today 68 (2001) 53–61

CATALYSIS TODAY

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# Catalytic activity of $CeO_2$–$ZrO_2$ mixed oxide catalysts prepared via sol–gel technique: CO oxidation

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## Abstract

$CeO_2$–$ZrO_2$ mixed oxide catalysts were prepared via a sol–gel technique and tested for carbon monoxide (CO) oxidation. Highly uniform nano-size solid solution particles of ceria–zirconia were attained under the conditions of this study (ca 100°C). The stabilization of the surface areas of the catalysts can be achieved by the addition of zirconium. The CO oxidation activity of the mixed oxides was found to be dependent on Ce/Zr ratio, which relates to the degree of reducibility. The catalytic activity for CO oxidation decreases with a decrease in Ce/Zr ratio. This might be due to the difference in phase compositions of the mixed oxides. It can be postulated that the cubic phase, fluorite structure, which is mainly found in $Ce_{1-x}Zr_xO_2$ (where $x < 0.5$) could be reduced easily than the tetragonal phase found in $Ce_{1-x}Zr_xO_2$ (where $x > 0.5$). Among the mixed oxide catalysts, $Ce_{0.75}Zr_{0.25}O_2$ was reported to exhibit the highest activity for CO oxidation.

*Keywords:* Carbon monoxide oxidation; Ceria–zirconia; Solid solution; Sol–gel

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## 1. Introduction

Ceria and Ce-containing mixed oxides have attracted much attention as oxidation catalysts because of their unique redox properties and high oxygen storage capacity. It has been reported that ceria has potential uses for the removal of post-combustion pollutants and of high strength organics from wastewater (catalytic wet oxidation) [1,2]. However, pure $CeO_2$ is seldom used since it is known to have poor thermal stability [3–6]. A loss in surface area also occurs due to the changes in pore structure and in crystallite growth. Doping with other rare earth or transition metal oxides [2,7,8] may improve the stability of the surface area of ceria at high temperature. However, the improvement is found to be insignificant.

Recently, there is much interest in a new generation of mixed oxide containing $CeO_2$ and $ZrO_2$ [9–19]. It has been reported that the addition of $ZrO_2$ to ceria leads to improvements in ceria's oxygen storage capacity, redox property, thermal resistance and better catalytic activity at lower temperature [19–21]. This was found to be due to the partial substitution of $Ce^{4+}$ with $Zr^{4+}$ in the lattice of ceria, which results in a solid solution formation [19,22]. It was suggested that the role of zirconia is to control the structure or the sites of ceria crystallisate [21].

Many preparation methods have been applied for the preparation of $CeO_2$–$ZrO_2$ solid solution for catalytic applications. These include the high-temperature firing or high-energy milling of a mixture of the oxides,

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PII: S0920-5861(01)00322-4

conventional precipitation, and sol–gel techniques [19,20]. Among these methods, sol–gel was found to be very beneficial since it yields products with high purity, homogeneity, well-controlled properties, and low temperature processing. The properties of the final products were found to be dependent on the temperature and the hydrolysis catalysts [23–25].

In this paper, the CO oxidation on $CeO_2$–$ZrO_2$ mixed oxides prepared via sol–gel technique using urea as a hydrolysis catalyst was studied. The effects of preparation conditions of mixed oxides and the mole ratio of $CeO_2$ and $ZrO_2$ upon the CO oxidation activity were investigated.

## 2. Experimental

### 2.1. Synthesis

$CeO_2$–$ZrO_2$ mixed oxide catalysts were prepared by using the sol–gel technique. Cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$ (99.0%), Fluka), and zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$ (99.0%), Fluka) were used as sources of Ce and Zr, respectively. The starting solution was prepared by mixing 0.1 M of metal salt solutions with 0.4 M of urea solution at a 2 to 1 volumetric ratio. The ratio between each metal salt was altered depending on the desired solid solution concentration: $Ce_{1-x}Zr_xO_2$,where $x = 0$, 0.25, 0.50, 0.75 and 1.0. The solution was kept at 100°C for either 50 or 120 h. The sample was then allowed to cool to room temperature before being centrifuged to separate the solid product from the solution. The solid product was washed with ethanol to prevent an agglomeration of the particles, and then dried overnight in an oven at 110°C followed by calcination at either 500 or 900°C for 4 h in air.

### 2.2. Characterization technique

Specific surface areas were determined by $N_2$ adsorption at 77 K (five point Brunauer–Emmett–Teller (BET)) method using a Quantachrome Corporation Autosorb. Prior to the analysis, the samples were outgassed at 250°C for 4 h. The morphology of the samples was also investigated under a scanning electron microscope (SEM) and transmission electron microscope (TEM).

The structure of the mixed oxides was examined by X-ray diffraction (XRD) on a Rigagu X-ray diffractometer system equipped with a RINT 2000 wide-angle goniometer using Cu Kα radiation and a power of 40 kV × 30 mA. The intensity data were collected at 25°C over a $2\theta$ range of 20–80°. FT-Raman measurement was used to confirm the fluorite structure of the mixed oxides. The spectra were measured using a Perkin Elmer 2000 FT Raman Spectrometer with a diode pumped YAG laser and a room temperature super InGaAs detector. The laser power was ca. 460 mW. A frequency of 100–4000 $cm^{-1}$ was observed.

### 2.3. Temperature-programmed reduction

Temperature-programmed reduction (TPR) of the catalyst was carried out using 5% hydrogen in nitrogen as a reducing gas on a Micromeritics TPD/TPR 2900 equipped with a thermal conductivity detector. The gas flow rate was 50 ml/min. Typically 20 mg of fresh catalyst was used in each experiment. Sample pretreatment was achieved by flowing He over the sample at 120°C for 4 h prior to each analysis.

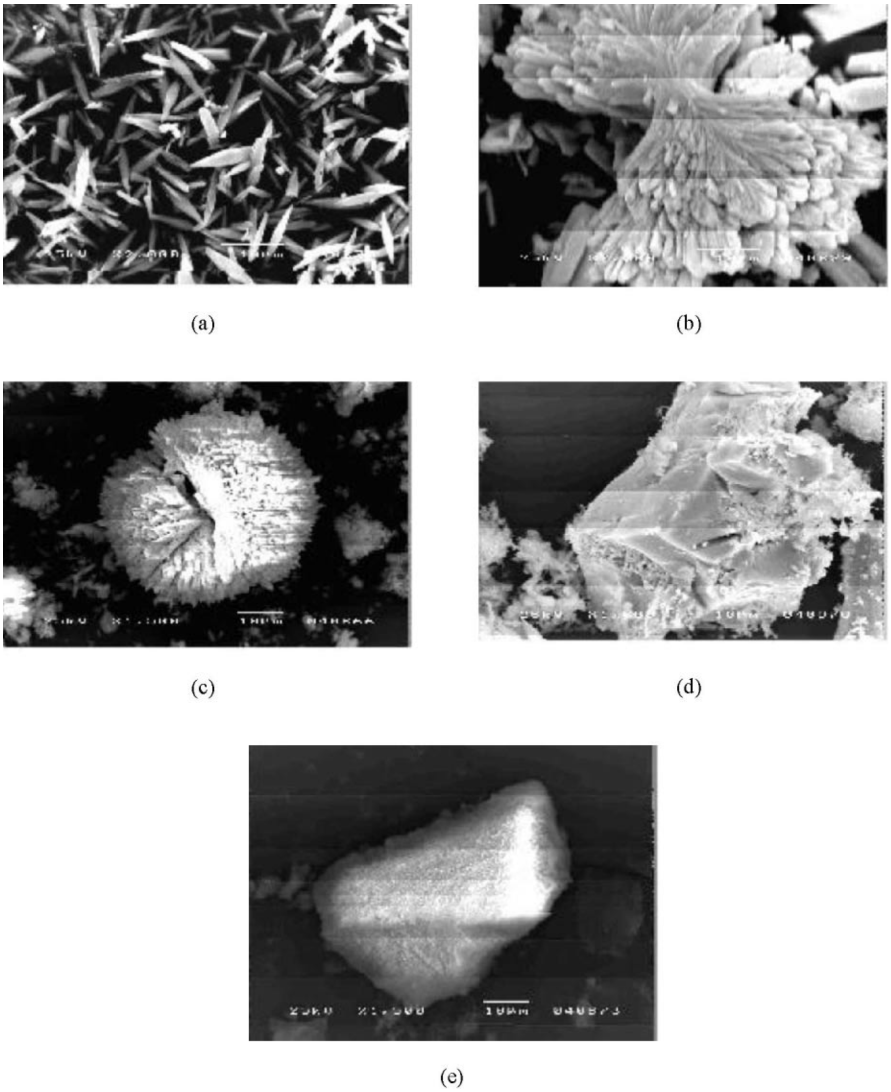
### 2.4. Activity test

Catalytic oxidation of carbon monoxide (CO) on mixed oxide catalysts was carried out in a differential packed bed quartz U-tube reactor (ID 4 mm) mounted in the constant temperature (±1 K) zone of an electric furnace. A mixed oxide sample of 0.1 g was packed between two layers of glass wool. Small diameter thermocouples were located before, in and after the catalyst bed. Exit gases were analyzed chromatographically using a Hewlett Packard 5890 series II fitted with a Carbosphere, 80/100 mesh, 10 ft × $\frac{1}{8}$ in., stainless steel packed column. Initial experiments were focused on the determination of “light-off” temperatures. Unless otherwise stated, regulated gas mixtures (50 ml/min) containing 1.0% CO and 1.0% $O_2$ (balance helium) were passed through the catalyst bed at ambient temperature. After stabilization, the temperature of the bed was raised at 5°C/min until oxidation was initiated, as shown by a temperature rise across the bed and by the conversion of CO. The light-off temperature was recorded as the temperature at which the conversion of CO reached 50%.

## 3. Results and discussion

### 3.1. BET, SEM and TEM characterization

The approach we used for the preparation of a mixed oxide solid solution of ceria–zirconia was a sol–gel technique using urea as the hydrolysis catalyst. The results showed that the mixed oxide catalysts prepared by this method are highly uniform. As shown in Fig. 1, pure $CeO_2$ particles are mainly of long thin needle shaped morphology. The aggregation of the primary long thin needle shaped particles was found in the case of zirconia-doped ceria particles. It was noticed that there was no effect of reaction time (reflux time) on the morphology of the catalysts. Interestingly, as shown in Fig. 2, nano-sized particles were achieved under the conditions of this study. The particle sizes of all mixed oxides are varied from 5 to 6 nm after

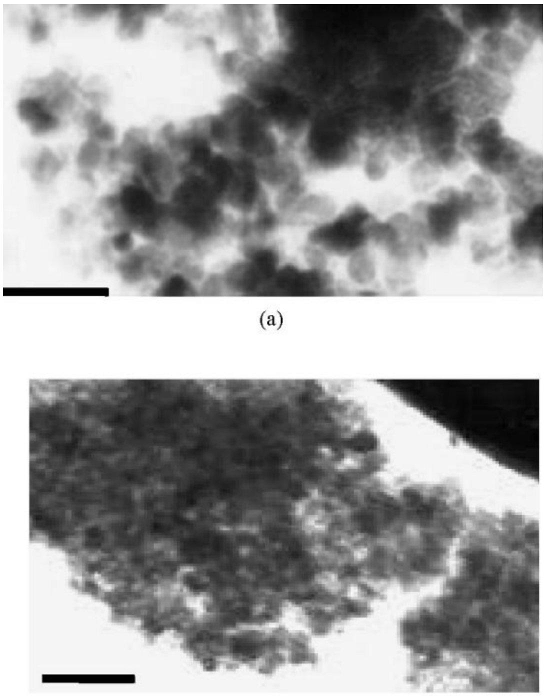


(a) (b)

(c) (d)

(e)

Fig. 1. SEM images of $Ce_{1-x}Zr_xO_2$ mixed oxide catalysts with the reflux time = 120 h, and calcined at 500°C: (a) $CeO_2$, (b) $Ce_{0.75}Zr_{0.25}O_2$, (c) $Ce_{0.50}Zr_{0.50}O_2$, (d) $Ce_{0.25}Zr_{0.75}O_2$, and (e) $ZrO_2$.



(a)

(b)

Fig. 2. TEM images of $Ce_{1-x}Zr_xO_2$ mixed oxide catalysts with the reflux time = 120 h, and calcined at 500°C: (a) $Ce_{0.50}Zr_{0.50}O_2$, (b) $Ce_{0.75}Zr_{0.25}O_2$.

calcinations at 500°C. The particle size was found to increase with an increase in calcination temperature (ca 9–10 nm at 900°C).

Apart from the homogeneity of the particles the sol–gel technique also yields particles, which possess high surface area. The BET surface areas of mixed oxide catalysts are summarized in Tables 1 and 2. The effect of reflux time on the surface areas is not pronounced. A slight increase in surface areas was achieved after longer reflux time was achieved. This might be due to a crystal nucleation-growth process during the reflux process [25]. The results also suggested that the addition of zirconium enhances the stability of the surface areas of the catalysts. It was found that the surface areas of the mixed oxides are higher than the surface area of pure ceria. This might be due to the fact that the crystallite growth process is retarded or disfavored by the incorporation of zirconium ions into the $CeO_2$ matrix enhancing the thermal stability of the mixed oxide catalysts. However, at high temperature (ca 900°C), the effect of zirconium ions was found to be minimized. The surface areas of all oxide samples were found to decrease drastically.

### 3.2. X-ray diffraction (XRD) and FT-Raman spectroscopy

Typical XRD patterns of the mixed oxides (indexed in the cubic Fm3m space group) are shown in Fig. 3. It is apparent that the patterns consist of six main reflections, typical of a cubic, fluorite structure of $CeO_2$, corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), and (4 0 0) planes. The results suggested that $Ce_{1-x}Zr_xO_2$ preferably crystallizes into

Table 1
BET surface areas of catalysts with the reflux time = 50 h

| Calcination temperature (°C) | $N_2$ BET surface area ($m^2/g$) | | | | |
|---|---|---|---|---|---|
| | Ce:Zr ratio = 100:0 | Ce:Zr ratio = 75:25 | Ce:Zr ratio = 50:50 | Ce:Zr ratio = 25:75 | Ce:Zr ratio = 0:100 |
| 500 | 101.6 | 108.4 | 116.0 | 120.1 | 79.0 |
| 900 | 4.6 | 9.2 | 12.5 | 21.3 | 12.2 |

Table 2
BET surface areas of catalysts with the reflux time = 120 h

| Calcination temperature (°C) | $N_2$ BET surface area ($m^2/g$) | | | | |
|---|---|---|---|---|---|
| | Ce:Zr ratio = 100:0 | Ce:Zr ratio = 75:25 | Ce:Zr ratio = 50:50 | Ce:Zr ratio = 25:75 | Ce:Zr ratio = 0:100 |
| 500 | 105.1 | 115.1 | 125.3 | 133.7 | 86.3 |
| 900 | 6.7 | 9.6 | 28.6 | 34.1 | 33.5 |

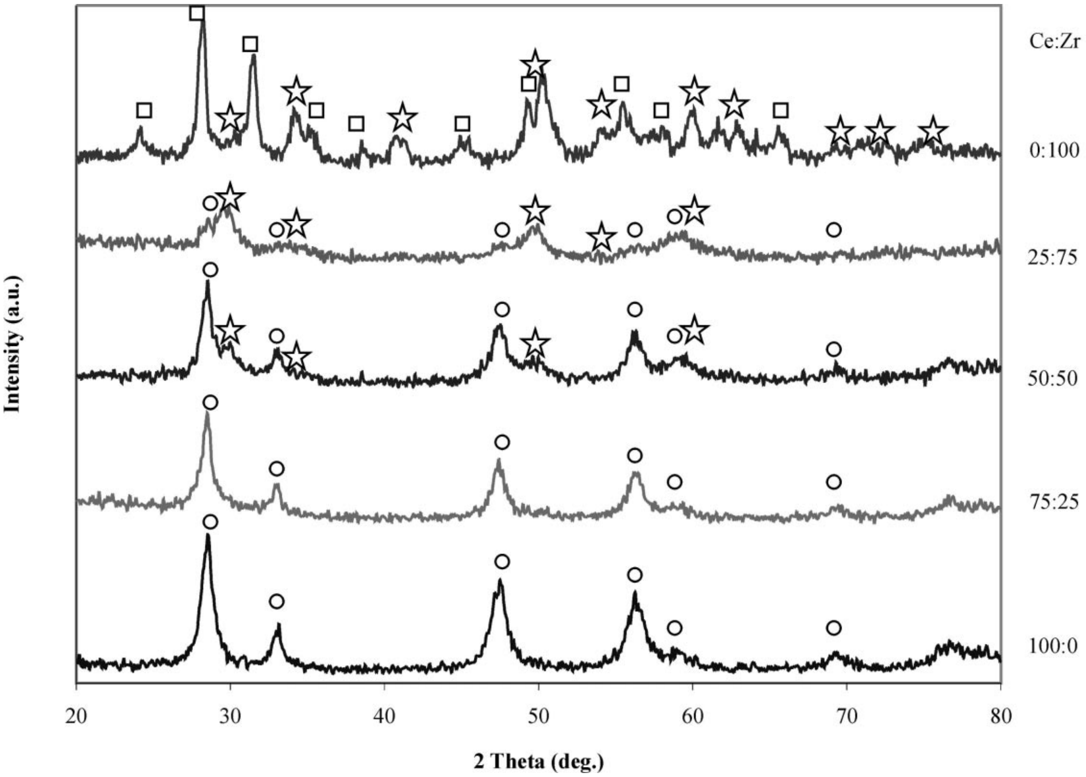


Fig. 3. XRD patterns for $Ce_{1-x}Zr_xO_2$ mixed oxide catalysts with the reflux time = 120 h, and calcined at 500°C: (○) cubic phase; (☆) tetragonal phase, and (□) monoclinic phase.

a cubic structure if $x$ is equal to or lower than 0.5. The presence of only the cubic phase in the samples ($Ce_{1-x}Zr_xO_2$,where $x < 0.5$) indicates that Ce and Zr are highly homogeneously distributed. The lack of free $ZrO_2$ in these samples is also confirmed by Raman spectroscopy.

Conversely, the evidence of a tetragonal phase was found when $x$ is higher than 0.5 and the presence of a monoclinic phase is also observed at a higher $ZrO_2$ content. It should be noted that the monoclinic phase is preferable at high temperatures (900°C in this study). A similar finding was reported elsewhere [10,20]. It should also be noted that the effect of reflux time on the structure of these oxides is insignificant. The XRD patterns of the samples are nearly identical. It was, however, found that peak intensity of the sample calcined at 900°C is higher than that of the sample calcined at 500°C. A difference in peak intensity may originate from the different degree of crystallinity of $CeO_2$ and ceria–zirconia.

The Raman spectra of the $Ce_{1-x}Zr_xO_2$ are shown in Fig. 4. It was found that in the case of ceria rich samples, $Ce_{1-x}Zr_xO_2$ (where $x \leq 0.5$), there is only one strong adsorption peak centered at about 456 $cm^{-1}$ typical of the $F_{2g}$ Raman active mode of a fluorite structured material. No evidence of pure $ZrO_2$ adsorption peaks was found in these samples. The results are in good agreement with the XRD analysis, which also indicates only the cubic, fluorite structure type. However, the absence of the adsorption peak at 456 $cm^{-1}$ was found in the zirconia rich samples $Ce_{1-x}Zr_xO_2$ (where $x > 0.5$). This suggested the phase transformation of the cubic phase to the tetragonal phase [26].

### 3.3. TPR

TPR studies were carried out over mixed oxide catalysts. Typical reduction behavior of $Ce_{1-x}Zr_xO_2$ mixed oxide is shown in Fig. 5. The results showed

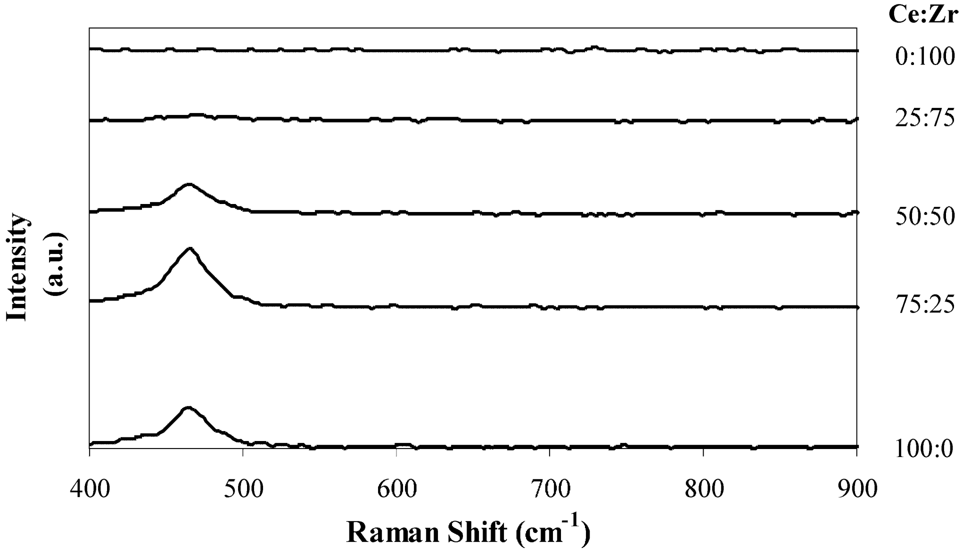


Fig. 4. Raman spectra of $Ce_{1-x}Zr_xO_2$ mixed oxide catalysts with the reflux time = 120 h, and calcined at 500°C.

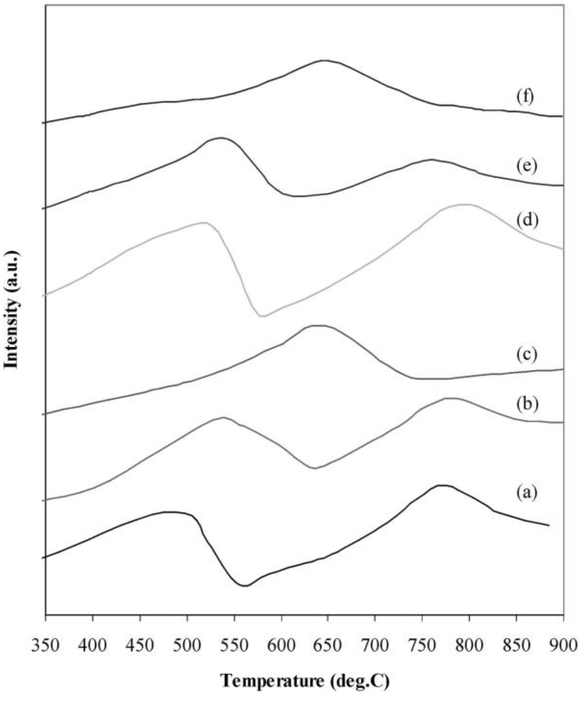


Fig. 5. TPR profile of $Ce_{1-x}Zr_xO_2$ mixed oxide catalysts calcined at 500°C with reflux time = 50 h, ($x = 0.25$ (a), 0.50 (b), 0.75 (c)) and with reflux time = 120 h ($x = 0.25$ (d), 0.50 (e), 0.75 (f)). A reducing gas contains 5% hydrogen in nitrogen and using a heating rate of 10°C/min. The gas flow rate was 50 ml min$^{-1}$.

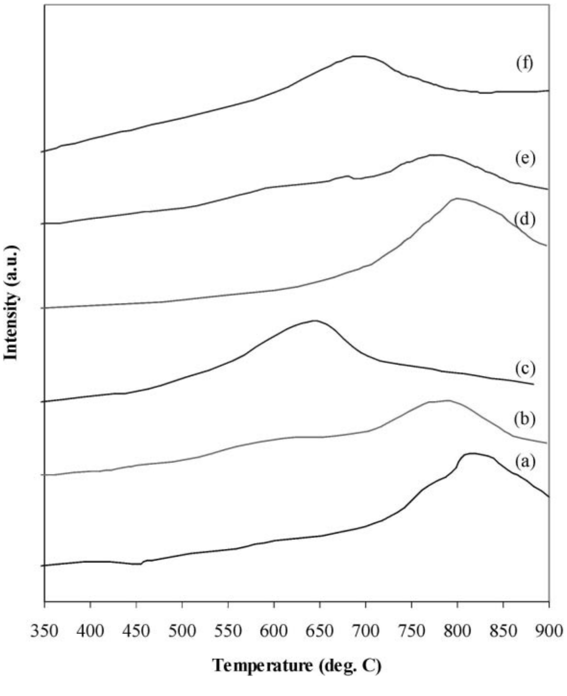


Fig. 6. TPR profile of $Ce_{1-x}Zr_xO_2$ mixed oxide catalysts calcined at 900°C with reflux time = 50 h ($x = 0.25$ (a), 0.50 (b), 0.75 (c)), and with reflux time = 120 h ($x = 0.25$ (d), 0.50 (e), and 0.75 (f)). A reducing gas contains 5% hydrogen in nitrogen and a heating rate of 10°C/min. The gas flow rate was 50 ml min$^{-1}$.

that the reduction behavior of $Ce_{1-x}Zr_xO_2$ mixed oxide catalysts prepared from different reflux time and calcined at 500°C is nearly identical. There are two peaks observed at low temperature and high temperature for $Ce_{1-x}Zr_xO_2$ mixed oxides ($x \leq 0.5$). While the peak at low temperature was understood as surface reduction, another peak at high temperature is the reduction of the material in the bulk [1,22,27–30]. The results indicated that $H_2$ consumption in the low temperature region shifted to higher temperature with the increasing Zr content as found in the case of $Ce_{0.25}Zr_{0.75}O_2$. As a consequence, we speculate that this shift in the low temperature region is a result of the irreducible structure of the material caused by high Zr content. It should be pointed out that the structure of $Ce_{0.25}Zr_{0.75}O_2$ is dominated by tetragonal phase, whilst the structure of $Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.5}Zr_{0.5}O_2$ is mainly in cubic phase. This may suggest that the tetragonal phase is more difficult to reduce.

The reflux time was still found to have an effect on the reducibility behavior of $Ce_{1-x}Zr_xO_2$ mixed oxide calcined at 900°C. As shown in Fig. 6, the absence of the low temperature region is due to the significant decrease in the surface areas of the mixed oxides. This also results in the decrease in the reducibility of the mixed oxides.

### 3.4. CO oxidation

The studies were focused on the measurement of the oxidation of CO over the mixed oxide catalysts: $Ce_{1-x}Zr_xO_2$ ($x = 0.25$, 0.5 and 0.75). Catalytic oxidation is known to be influenced by mass transfer at high conversions, and comparisons of activity were made in terms of “light-off”. It is convenient to define the “light-off” temperature as the temperature when the conversion reaches either 10% or, as in this case, 50%.

Initial experiments were carried out to compare the CO oxidation activity of the mixed oxides calcined at either 500 or 900°C. The results showed that the activities of the mixed oxides calcined at 900°C are incomparable to those of mixed oxides calcined at 500°C. CO oxidation could not be achieved at a temperature below 500°C. This might be due to the fact that surface areas and reducibility of the mixed oxides calcined at 900°C are considerably lower compared

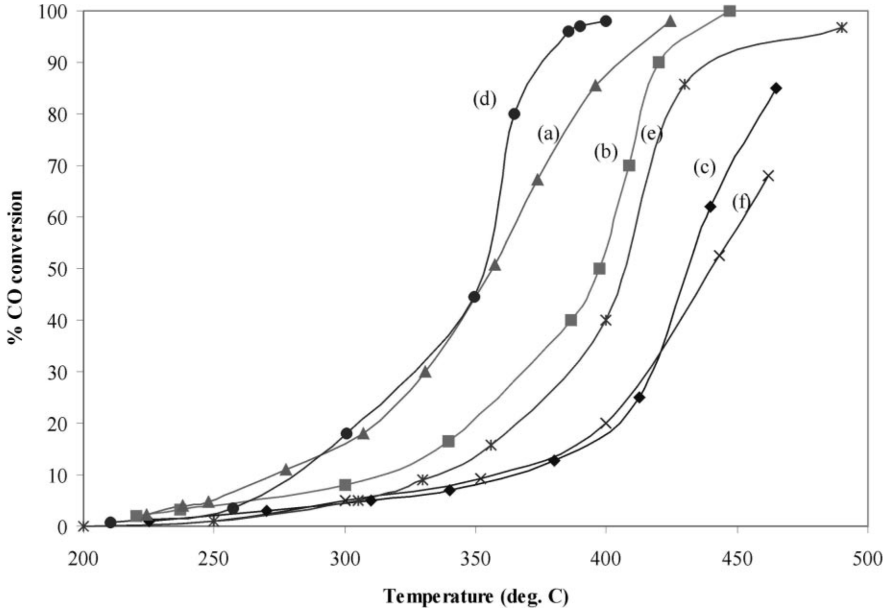


Fig. 7. Light-off curves over $Ce_{1-x}Zr_xO_2$ mixed oxide catalysts prepared via sol–gel technique with reflux time = 50 h ($x = 0.25$ (a), 0.50 (b), and 0.75 (c)) and 120 h ($x = 0.25$ (d), 0.50 (e), and 0.75 (f)) and calcined at 500°C. Gas mixture contains 1.0% CO, 1.0% $O_2$ and balance He. Total flow: 50 ml $min^{-1}$.

to that of mixed oxides calcined at 500°C as discussed earlier. Thus, it is our intention not to further investigate the catalytic activities of the mixed oxides calcined at 900°C.

Fig. 7 shows the light-off temperatures of mixed oxide catalysts at different preparation conditions. It was found that the reflux time has no effect on the CO oxidation activities of mixed oxide catalysts. For example, the light-off temperatures of $Ce_{0.75}Zr_{0.25}O_2$ prepared via 50 or 120 h reflux time are nearly identical. This also applies in the case of $Ce_{0.5}Zr_{0.5}O_2$and $Ce_{0.25}Zr_{0.75}O_2$. This might be due to the fact that the characteristics (BET, XRD, FT-Raman and TPR) of the mixed oxides prepared via 50 or 120 h reflux time are nearly indistinguishable.

The catalytic activity of mixed oxide catalysts was found to be a function of Ce/Zr ratio. The CO oxidation activities of the catalysts were found to decrease with a decrease in Ce/Zr ratio with $Ce_{0.75}Zr_{0.25}O_2$ exhibiting the highest activity for CO oxidation. It should be pointed out that the catalytic activity has no direct correlation with surface areas. Although $Ce_{0.75}Zr_{0.25}O_2$ possesses a lower surface area than $Ce_{0.5}Zr_{0.5}O_2$ and $Ce_{0.25}Zr_{0.75}O_2$, it demonstrates the highest activity for CO oxidation. It has been suggested that the activity of the ceria–zirconia mixed oxides is closely related to their reducibility [20,21]. In our study, it was found that $Ce_{0.75}Zr_{0.25}O_2$ is the easiest reducible catalyst followed by $Ce_{0.5}Zr_{0.5}O_2$ and $Ce_{0.25}Zr_{0.75}O_2$ mixed oxide catalysts, respectively. Hence, the highest activity of $Ce_{0.75}Zr_{0.25}O_2$ for CO oxidation is expected.

## 4. Conclusion

It can be concluded that the highly uniform nano-size solid solution particles of ceria–zirconia can be prepared via sol–gel technique using urea as the hydrolysis catalyst. The effect of reflux time on the characteristics of the mixed oxides was not prominent. The stabilization of surface areas of the catalysts can be achieved by the addition of zirconium. However, it was found that the effect of zirconium was almost demolished under high temperature treatment (900°C).

The CO oxidation activity of the mixed oxides was found to be dependent on Ce/Zr ratio. It was found that the activity decreases with a decrease in Ce/Zr ratio. Due to high reducibility, the $Ce_{0.75}Zr_{0.25}O_2$ solid solution was reported to have the highest activity among mixed oxide catalysts. It might be postulated that the cubic phase fluorite structure of $Ce_{1-x}Zr_xO_2$ is found mainly in the case where $x$ is less than 0.5 could be reduced easily than the tetragonal phase. It is evident that $Ce_{0.25}Zr_{0.75}O_2$ contains a mixed phase between cubic and tetragonal phases, which might result in a decrease in the degree of reducibility. This phase segregation was also observed elsewhere [12]. The presence of tetragonal phase was also noticed in the $Ce_{0.5}Zr_{0.5}O_2$, but not to a great extent. This might be the reason why the catalytic activity of $Ce_{0.5}Zr_{0.5}O_2$ is lower than that of $Ce_{0.75}Zr_{0.25}O_2$. It might be speculated that a solid solution of ceria–zirconia in a cubic phase is a good catalyst for CO oxidation. The presence of tetragonal phase should be avoided in order to achieve high catalytic activities.

## Acknowledgements

The authors would like to thank the Petroleum and Petrochemical College and Thailand Research Fund (grant number PDF/38/2541) for their financial support.

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