Effect of support modification on reduction and CO oxidation activity of doped ceria-supported copper oxide catalyst

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Ceria materials were modified by doping with gadolinia or yttria and by a hold period at 260 °C for 2 h during temperature-programmed calcinations to 650 °C. These doped ceria-supported copper oxide catalysts and the doped ceria material were characterized by temperature-programmed reduction, electron paramagnetic resonance, and CO oxidation activity test. It was observed that, as the doping concentration of gadolinia increases, the reduction temperature of the copper oxide species increases and the CO oxidation activity decreases. This is due to increased formation of the surface spinel species of copper oxide with gadolinia. As the yttria content increases to greater than 10 mol%, surface segregation occurs, which causes the amount of surface oxygen vacancies to decrease. It was also found that maintaining the temperature at 260 °C during calcination may decrease the amount of oxygen vacancies. The surface oxygen vacancies may be the active sites for CO oxidation over the oxygen ion conducting materials in the absence of any metal present. Gd doping leads to the formation of extrinsic oxygen vacancies, which increases the oxygen ionic conductivity of the doped ceria and thus increases the CO oxidation activities of the supported catalysts as well as of the doped ceria.

KEY WORDS: support; modification; reduction; CO oxidation; doped ceria; copper oxide.

1. Introduction

In heterogeneous catalytic reactions, the support was usually considered as an inert material before the concept of a strong metal–support interaction was proposed [1,2]. This concept emphasized the importance of the support characteristics on the catalytic activities. Also, the concept of an interfacial metal–support interaction (IMSI) was proposed [3]; specifically, metal oxide species supported on oxygen ion conducting materials show a remarkable effect on the activity enhancement for CO oxidation [4]. With these concepts, support modifications have attracted much research interest and are considered an important factor in improving catalytic activity [5,6].

Sanchez and Gazquez [7] have pointed out that a support with a fluorite structure offers surface oxygen vacancies to promote metal dispersion, sintering resistivity, and catalytic activity. Dow *et al.* [4,8] reported that, with the oxygen ion conducting YSZ (yttria-stabilized zirconia) as a support, the reduction temperature of copper oxide species is much lower than when supported on alumina and they attributed this to the IMSI effect between the surface oxygen vacancies and the copper oxide species.

For CO oxidation, Dow and Huang [9] reported that the catalytic activity of the CuO catalyst can be significantly enhanced by the YSZ support, which leads to the supported copper oxide exhibiting a precious metal-like catalytic behavior. The activity enhancement of the YSZ-supported CuO is attributed to the surface oxygen vacancies of YSZ support by means of the formation of interfacial active centers. Wang *et al.* [10] elucidated the effect of oxygen vacancies of the support on the activity enhancement and light-off behavior of CO oxidation over samaria-doped ceria-supported CuO catalysts. They considered this activity enhancement to be due to the IMSI.

In this work, the effects of support modifications on the reduction behavior and the CO oxidation activity of doped ceria-supported copper oxide catalysts were studied. The support modifications were carried out by doping gadolinium or yttrium ions into ceria with a co-precipitation method to produce extrinsic oxygen vacancies. A variation of the calcination condition was also carried out by allowing the doped ceria to be maintained at 260 °C for 2 h during the temperature-programmed heating process. This procedure was used to induce a change of the support characteristics. Results showed that these modifications of the support materials indeed lead to distinguishable effects on the reduction characteristics and the CO oxidation activities not only for the doped ceria-supported CuO catalysts but also for the doped ceria materials.

2. Experimental

2.1. Support and catalyst preparation

Gadolinia-doped ceria (GDC) was prepared from reagent-grade metal nitrates $Gd(NO_3)_3 5H_2O$ (99.9%

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purity, Strem Chemicals Inc., USA) and $Ce(NO_3)_3 \cdot 6H_2O$ (99.5% purity, Strem) by a co-precipitation method. Appropriate amounts of gadolinia nitrate and cerium nitrate were dissolved in deionized water. Hydrolysis of the metal salts to hydroxides was obtained by adding NH_4OH solution while stirring the solution to keep the pH at about 11. A filtration step with suction was carried out twice to remove the NH_4OH solution. After filtration, the gel was dried at 120 °C for 24 h. Then, the dried cake was ground to a powder and put into a calcination system. The sample was then calcined in flowing air at 1 L/min with a heating rate of 10 °C/min to 650 °C, and kept at 650 °C for 4 h before being cooled naturally (annealed). Some samples were heated to 260 °C and maintained at that temperature for 2 h during the temperature-programmed heating process. The samples referred to in this work are those not treated by maintaining the temperature at 260 °C during calcination, except as noted specifically.

Yttria-doped ceria (YDC) was prepared from $Y(NO_3)_3 \cdot 6H_2O$ (99.9% purity, Strem). The preparation method was the same as that for gadolinia-doped ceria as described above.

The copper catalysts were prepared by impregnating GDC or YDC support with an appropriate amount of aqueous solution of copper nitrate $Cu(NO_3)_2 \cdot 3H_2O$ (99.999% purity, Strem). After evaporating excess water at 80 °C, the sample was dried at 120 °C for 12 h. Then, the sample was ground to a powder and put into a calcination system. The sample was then calcined in flowing air at 1 L/min with a heating rate of 10 °C/min to 260 °C, and maintained at 260 °C for 1.5 h. It was then heated to 500 °C and kept there for 3.5 h before being cooled naturally.

As regards notation, the number before GDC or YDC is the gadolinia or yttria content in mol%, which is evaluated based on the moles of gadolinium or yttrium plus cerium. The loading of copper metal in this work is always 1 wt%.

2.2. Temperature-programmed reduction

Temperature-programmed reduction (TPR) was carried out by using 10% hydrogen in nitrogen as a reducing gas in a conventional TPR reactor. The reactor was made up of an 8 mm I.D. quartz U-tube with sample of 200 mg mounted on loosely packed quartz wool. The outlet of the reactor was connected to a glass column packed with molecular sieve 5A in order to remove the moisture produced from reduction. The flow rate of the reducing gas was kept at 30 mL/min by a mass flow controller. The temperature of the reactor was raised from room temperature to 800 °C at a rate of 10 °C/min by a temperature-programmable controller (Eurotherm, Model 815P). The rate of hydrogen consumption was measured by a thermal conductivity detector and recorded by an on-line personal computer. The peak areas of TPR were separated and integrated by this computer using special software.

2.3. Electron paramagnetic resonance

Electron paramagnetic resonance (EPR) analysis was employed to characterize the structure of ceria. The EPR measurement was conducted at −196 °C with a Bruker 200D spectrometer operating in X-band (~9.7 GHz). Before the measurement, the sample was dried in air at 120 °C for 24 h. The magnetic field was modulated at 1000 kHz. The g values were obtained by comparing with a diphenylpicrylhydrazyl (DPPH) standard ($g = 2.0036$).

2.4. Activity test

The steady-state activity of CO oxidation was measured under atmospheric pressure in a continuous flow reactor charged with 0.01 g of catalyst. The reactor was of an 8 mm ID Pyrex U-tube. A K-type thermocouple was inserted into the catalyst bed to measure the reaction temperature.

The reactant gas mixture was composed of 2% CO (99.9% purity, Air Products, USA) and 3% O_2 (99.995% purity) with the balance argon, at a total flow rate of 300 mL/min. The flow rates of CO, O_2, and argon were regulated by mass flow controllers (Model HFC-202, 0.1 mL/min accuracy, Hastings, USA). The reactor outflow was analyzed on-line by a CO-NDIR (Beckman 880), a gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector, and an oxygen analyzer (Beckman 755A). Both the signals of CO-NDIR and temperatures of the catalyst bed were transmitted to a Y-t recorder (Yokogawa, LR-4110).

3. Results and discussion

3.1. Temperature-programmed reduction

3.1.1. Effect of gadolinia doping

As shown in figure 1, the reduction temperature of the copper oxide species increases as the doping concentration of gadolinia increases. This is probably due to the segregation of the gadolinia species on the ceria surface [11], and also due to the formation of the surface spinel species of copper oxide with gadolinia [12]. It is noted that there is no peak occurring from the reduction of the gadolinia-doped ceria (GDC) species until a temperature of over 800 °C.

However, as shown in figure 2, for GDC without any metal loading, there is a peak occurring at around 530 °C in addition to the peak appearing at a temperature of over 800 °C. These two peaks of GDC are similar to

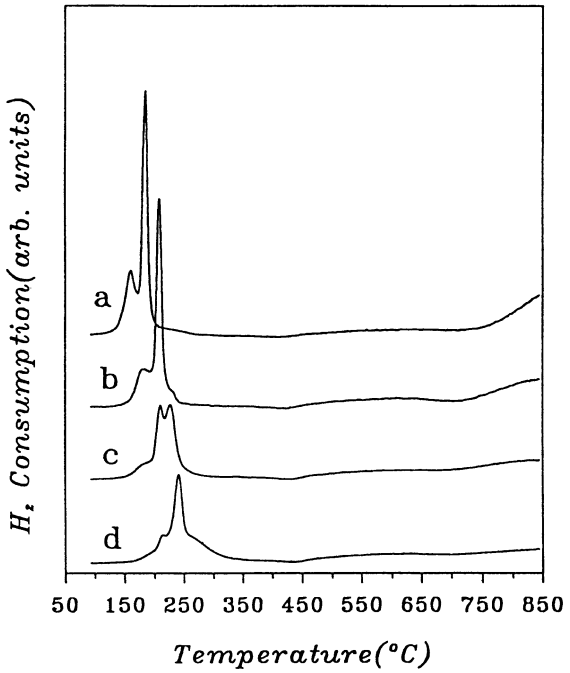

Figure 1. TPR profiles of gadolinia-doped ceria-supported CuO catalysts: (a) CuO/CeO_2, (b) CuO/5GDC, (c) CuO/10GDC, (d) CuO/15GDC.

those of ceria as reported by Yao and Yu Yao [13]. As pointed out by those authors, the 530 °C peak is due to the reduction of the surface capping oxygen of ceria and the over-800 °C peak is due to the reduction of the bulk ceria.

In addition, as also seen in figure 2, there is a peak at around 430 °C appearing as a shoulder to the left of the 530 °C peak. This shoulder peak varies with Gd content.

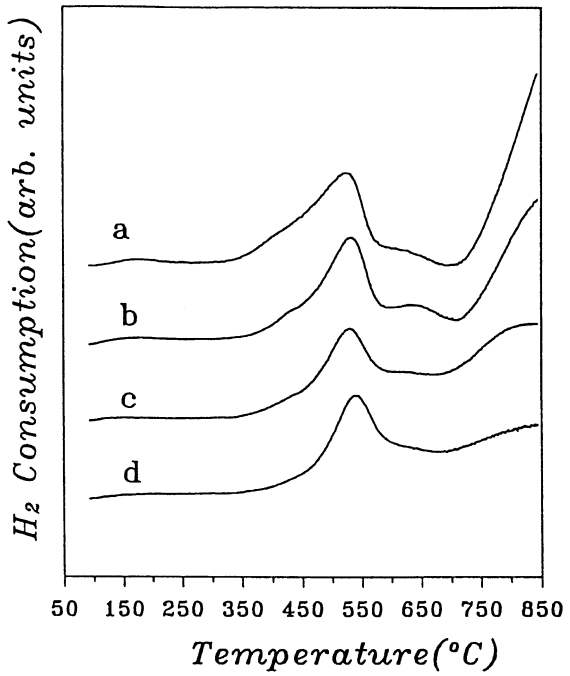

Figure 2. TPR profiles of gadolinia-doped ceria: (a) CeO_2, (b) 5GDC, (c) 10GDC, (d) 15GDC.

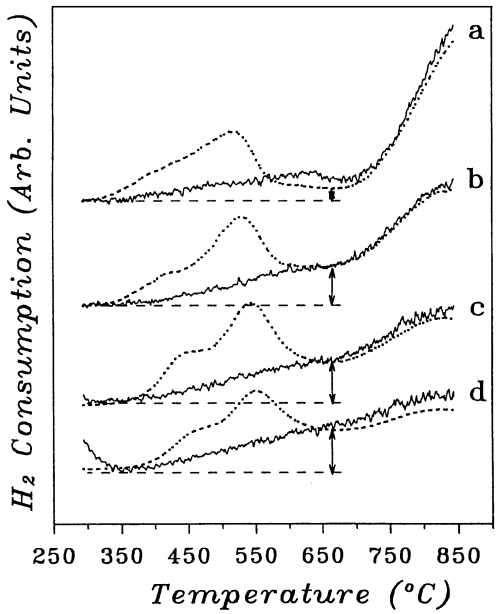

Figure 3. TPR profiles of yttria-doped ceria-supported CuO catalysts (solid lines) and yttria-doped ceria (dashed lines): (a) CeO_2, (b) 5YDC, (c) 10YDC, (d) 15YDC.

This phenomenon is more observable with yttria doping and is thus discussed in the next section.

3.1.2. *Effect of yttria doping*

As shown in figure 3, similar to GDC, the yttria-doped ceria (YDC) also shows a peak at around 530 °C when there is no metal loading. However, with the copper-loaded GDC, the 530 °C peak disappears. The existence of this phenomenon is proposed to be due to the surface capping oxygen becoming a shared oxygen on CuO/YDC. Note that the occurrence of the 530 °C peak is due to the surface capping oxygen. Since ceria is a non-stoichiometric oxide, its surface capping oxygen may exchange rapidly with gaseous oxygen. Thus, during calcination of Cu/YDC in air, the copper species may form copper oxide by bonding with the surface capping oxygen of YDC, and this oxygen atom becomes a shared oxygen between cerium and copper. These shared oxygen species are those associated with the copper oxide species which are reduced at temperatures below 300 °C, as shown in figure 4. This is the reason why the 530 °C peak occurring with the unloaded YDC disappears with the loaded YDC.

A comparison of figures 3 and 2 shows that the 430 °C shoulder peak of the unloaded YDC is larger than that of the unloaded GDC. Since the size of this peak varies with the yttria content and has a maximum value for 10YDC, its appearance is considered to be due to the interaction of the surface capping oxygen with the surface oxygen vacancy. Thus, as the doping content of yttria increases to increase the amount of the oxygen vacancies, this shoulder peak becomes larger. However, as the yttria content increases to greater than 10 mol%, surface

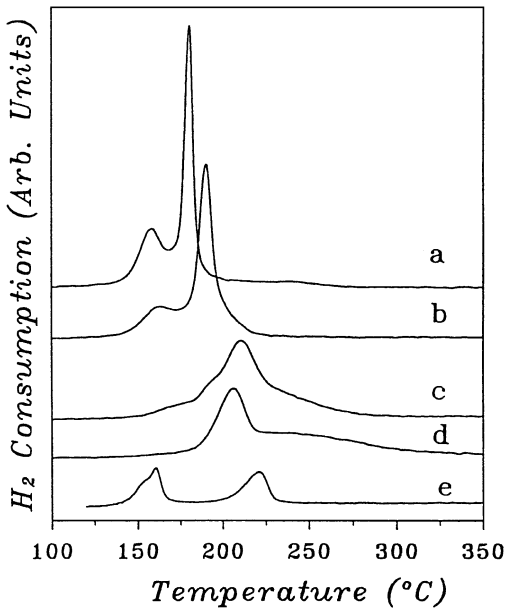

Figure 4. TPR profiles of yttria-doped ceria-supported CuO catalysts: (a) CuO/CeO_2, (b) CuO/5YDC, (c) CuO/10YDC, (d) CuO/15YDC, (e) CuO/8YSZ (scale ×2.5).

segregation may occur and cause the amount of the surface oxygen vacancies to decrease, and thus reduce the size of the shoulder peak. Therefore, the larger shoulder peak of YDC than that of GDC may be an indication that the amount of surface oxygen vacancies of YDC is higher than that of GDC.

As shown by the arrows in figure 3, the reduction of the bulk ceria occurs at a lower temperature as the doping content of yttria increases. This may be due to the interaction of the lattice oxygen of ceria with the bulk oxygen vacancies, the number of which increase with increasing yttria content. Nevertheless, this phenomenon of earlier reduction does not occur with those oxygen species which do not interact with the oxygen vacancy, and thus the TPR profile of the over-800 °C peak becomes flatter as the doping content of yttria increases. Note that the area under the curve corresponds to the amount of the oxygen species and the number of oxygen species not interacting with the oxygen vacancy decreases with increasing yttria content.

As shown in figure 4, the lowest-temperature peak of ceria is at almost the same temperature as that of 8YSZ (8 mol% yttria-stabilized zirconia). Since the lowest-temperature peak (called the α peak) of YSZ is due to the formation of the nested oxygen ion (NOI) on the YSZ surface [8], the formation of the α peak over ceria may also be due to NOI. The formation of NOI on the surface of ceria may be due to the existence of the Ce^{3+} species in the bulk ceria after 800 °C calcination [8,14] and thus due to the existence of the intrinsic oxygen vacancy in the bulk; these oxygen vacancies may migrate in the lattice and move to the surface to form NOI.

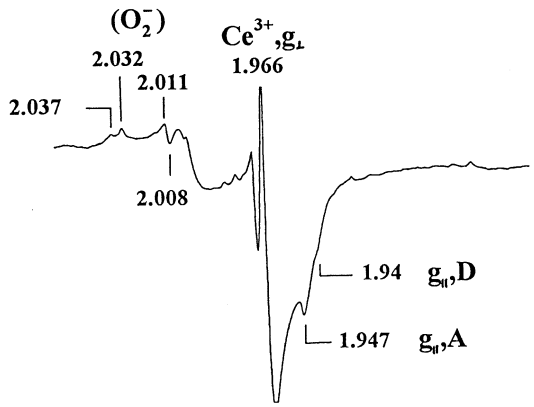

Figure 5. EPR profile for ceria with a hold period at 260 °C for 2 h during calcinations.

As also shown in figure 4, the lowest-temperature peak (α peak) moves to a higher temperature and also becomes smaller or even disappears as the doping of yttria increases. This is due to the decrease of the Ce^{3+} species and thus a decrease of oxygen vacancies with increasing yttria content [14]. A comparison of figures 4 and 1 shows that the effect of yttria doping into ceria on the shrinking of the α peak is higher than that of gadolinia doping. This may mean that the extent of the decrease of the Ce^{3+} species with increasing yttria content is higher than that with increasing gadolinia content. On the other hand, the effect of yttria doping on the shift of the α peak to a higher temperature is less than that of gadolinia doping. This is probably because of the formation of the surface spinel species of copper oxide with gadolinia, as noted in section 3.1.1.

3.1.3. *Effect of calcination conditions*

A modification of the oxygen ion conducting material was carried out by varying the calcination conditions, i.e., maintaining the sample at 260 °C for 2 h during the calcinations. It was observed that a hold period at 260 °C probably decreases the amount of oxygen vacancies. Dow [15] has reported EPR profile of ceria without a hold period at 260 °C; a comparison of his profile with the EPR profile in figure 5 indicates that the Ce^{3+} signal becomes weaker with a hold period at 260 °C, which means that the Ce^{3+} species in the bulk has been reduced with a hold period at 260 °C. This will cause the number of intrinsic oxygen vacancies to be reduced. As a consequence, the surface oxygen vacancies also become fewer and thus the size of the α peak shrinks. Note that the occurrence of the α peak is due to the interaction of the surface oxygen vacancy with the copper species [8]. The reason why a hold period at 260 °C may reduce the amount of Ce^{3+} species is considered to be due to the increased extent of the oxidation of $Ce(OH)_3$ to CeO_2 during the hold period at 260 °C for 2 h; thus, during the following calcination, the formation of the intrinsic oxygen vacancies decreases.

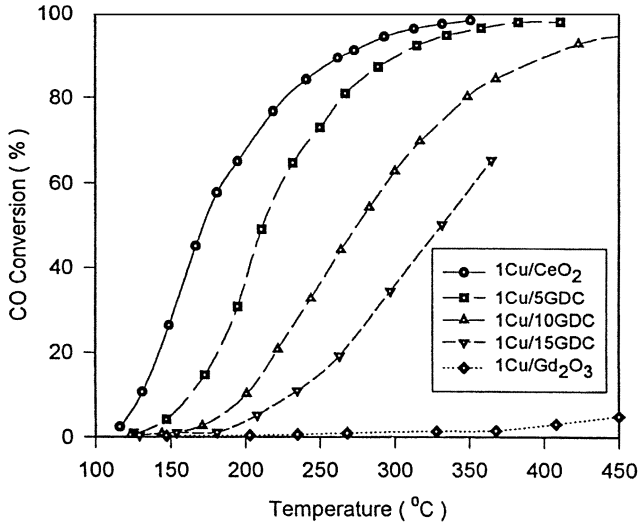

Figure 6. CO oxidation activities of CuO/GDC catalysts.

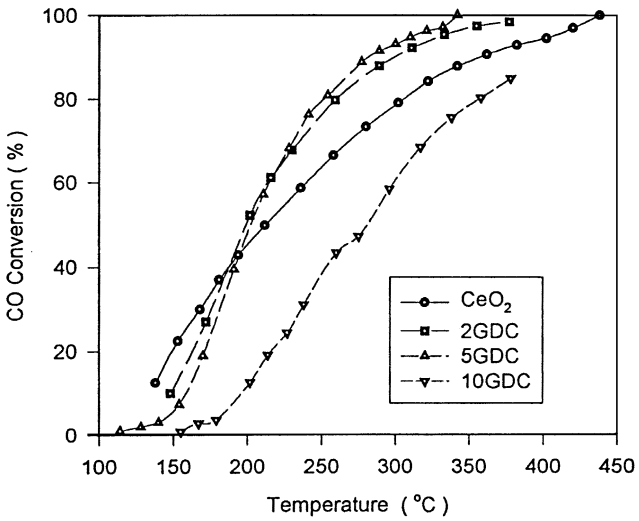

Figure 7. CO oxidation activities of CuO/GDC catalysts with the support hold at 260 °C for 2 h during calcinations.

3.2. CO oxidation activity

3.2.1. GDC-supported CuO catalyst

As shown in figure 6, with increasing Gd doping, the CO oxidation activity of the GDC-supported CuO catalyst decreases. This shows the same trend as that of the lowest-temperature peak (the α peak), whose temperature increases with increasing Gd doping, as shown in figure 1. Note that a higher α peak temperature corresponds to a lower CO oxidation activity for oxygen ion conducting material such as YSZ [9]. Also note that the surface areas of the supports are in the order 5GDC ($38.9\,m^2/g$) > CeO_2 ($32.5\,m^2/g$) > 10GDC ($26.6\,m^2/g$) > 15GDC ($25.8\,m^2/g$). It is seen that the difference in the surface area of the support would not affect the order of the CO activities as shown in figure 6, if such an effect of the support area existed for these low-loading (1 wt%) catalysts.

Figure 6 also shows that the Gd_2O_3-supported CuO catalyst has almost no activity. This is considered to be due to two factors. One is that Gd_2O_3 is not an oxygen ion conducting material and thus no active site with the interfacial metal oxide–support interaction (IMOSI) can be formed that would enhance the CO oxidation. This may be an indication of the importance of IMOSI and thus of the oxygen vacancies for CO oxidation. The other factor is that the surface spinel species of copper oxide with gadolinia has almost no activity for CO oxidation. This corresponds well with the fact that the formation of the surface spinel species of copper oxide with gadolinia will increase the α peak temperature, which means that the reduction of the surface species becomes more difficult and in turn means that the CO oxidation is also more difficult.

The effect of varying the calcination condition, i.e., by a hold period at 260 °C for 2 h during the calcination process, is shown in figure 7. As can be seen, with 2 to 5 mol% Gd doping and with increasing temperature, the CO oxidation activities of the CuO/GDC catalysts increase at a much faster rate than that of the CuO/CeO_2 catalyst and become higher than that of CuO/CeO_2 at about 190 °C. In addition, the activity of CuO/5GDC increases at a faster rate than that of CuO/2GDC and becomes higher than that of the latter at about 210 °C. This is considered to be due to the variation of the oxygen ionic conductivity with Gd doping.

As discussed in section 3.1.3, a hold period at 260 °C would decrease the amount of intrinsic oxygen vacancies. However, Gd doping should lead to the formation of extrinsic oxygen vacancies. Thus, increasing Gd doping should increase the amount of extrinsic oxygen vacancies and, as a consequence, increase the oxygen ionic conductivity.

On the other hand, Gd doping will increase the reduction temperature of the lowest-temperature peak (the α peak) as shown in figure 1. Since a higher α peak temperature corresponds to a lower CO oxidation activity for YSZ-supported copper oxide catalyst [9], similar behavior may occur for CuO/CeO_2 and CuO/GDC, and thus the CO oxidation activities are in the order CuO/CeO_2 > CuO/2GDC > CuO/5GDC > CuO/10GDC at temperatures below 190 °C, as shown in figure 7.

When the reaction temperature increases, the oxygen ion conductivity of the support also increases. This will increase the exchange rate of the oxygen species on the support surface and thus will enhance the CO oxidation activity. A higher oxygen ionic conductivity will lead to a higher exchange rate of the surface oxygen species and, as a consequence, increase the CO oxidation activity. As reported by Mogensen *et al.* [16], with 10 mol% Gd doping, the GDC material has the highest oxygen ionic conductivity. Since the catalyst only utilizes the surface characteristics of the material, surface segregation of gadolinia would make 5GDC better than 10GDC on

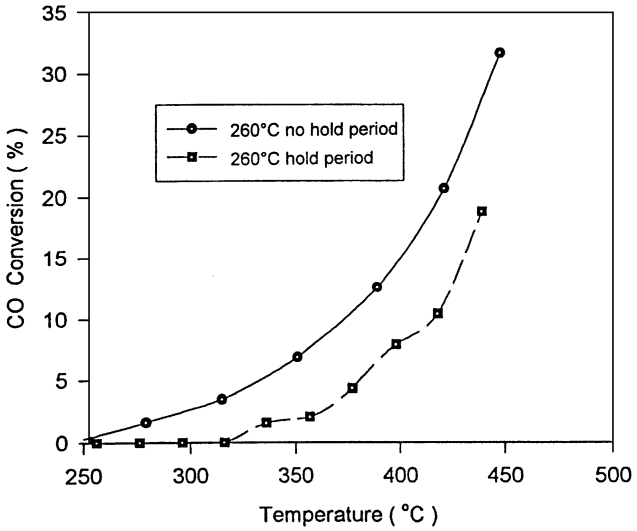

Figure 8. CO oxidation activities with ceria as catalysts.

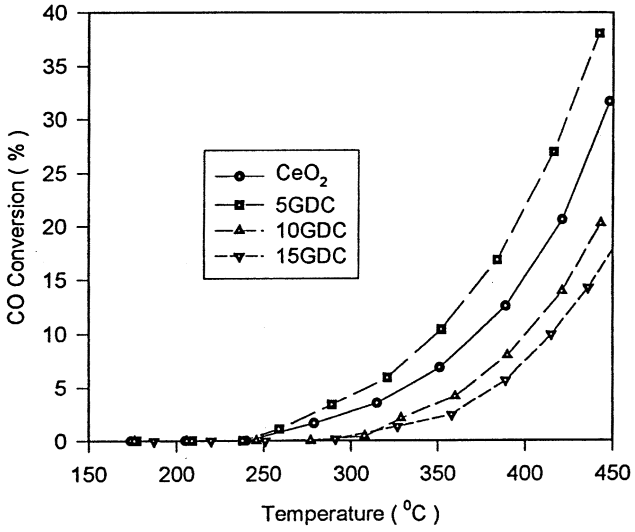

Figure 9. CO oxidation activities with gadolinia-doped ceria as catalysts.

the oxygen ionic conductivity at or near the surface. Tseng and Huang [17] have observed, by means of XPS, surface enrichment of samaria on samaria-doped ceria and reported an optimum dopant concentration for the methanol reforming reaction. They proposed that increasing dopant concentration over the optimum value will lead to increased defect interaction and result in a sharp reduction in mobility. Thus, the low activity of CuO/10GDC may be due to a sharp decrease in the oxygen ionic conductivity of 10GDC by surface segregation. In addition, the phenomenon that the activity of CuO/5GDC increases at a faster rate than that of CuO/2GDC with increasing reaction (operation) temperature indicates a higher activation energy for the oxygen ionic conductivity for 5GDC than that for 2GDC. In other words, the oxygen ionic conductivity of 5GDC is more temperature sensitive than that of 2GDC.

3.2.2. GDC as catalyst

A comparison of figures 6 and 7 shows that the CO oxidation activity of the CuO catalyst supported on GDC without a hold period at 260 °C during calcination is higher than that on GDC with a hold period at 260 °C. This behavior also occurs when the ceria material without any metal loading was used as the catalyst, as shown in figure 8. Since the effect of a hold period at 260 °C during calcination is probably due to a decrease of the amount of oxygen vacancies, as noted in section 3.1.3, the oxygen vacancies may be responsible for the occurrence of CO oxidation when an oxygen ion conducting material such as ceria was used as the catalyst. In other words, the surface oxygen vacancies may be the active sites for CO oxidation over the oxygen ion conducting materials.

As shown in figure 9, with 5 mol% Gd doping, the catalytic activity of GDC becomes higher than that of ceria. However, when the Gd doping is increased to 10 mol%, the catalytic activity decreases to be lower than that of ceria and the activity decreases further with more Gd doping. This shows that the oxygen ionic conductivity may be at work here. It is reasonable to expect that the same effect as that of the supported CuO catalyst occurs here, i.e., the CO oxidation activity increases as the oxygen ionic conductivity increases. As noted in section 3.2.1, 5GDC would have the highest oxygen ionic conductivity; thus, 5GDC would have the highest CO oxidation activity and this is confirmed by the results of figure 9. Therefore, it is confirmed that the formation of extrinsic oxygen vacancies increases the oxygen ionic conductivity and thus increases the CO oxidation activity.

4. Conclusions

Ceria materials were modified by doping with gadoinia or yttria and by a hold period at 260 °C for 2 h during temperature-programmed calcinations of these doped ceria-supported copper oxide catalysts and the doped ceria material. The following conclusions can be drawn:

1. As the doping concentration of gadolinia increases, the reduction temperature of the copper oxide species increases. This is due to an increased formation of the surface spinel species of copper oxide with gadolinia.
2. As the yttria content increases to higher than 10 mol%, surface segregation occurs which causes the amount of the surface oxygen vacancies to decrease.
3. A hold period at 260 °C for 2 h during calcination may decrease the amount of oxygen vacancies, which causes the CO oxidation activity to decrease.
4. The surface oxygen vacancies may be the active sites for CO oxidation over the oxygen ion conducting materials without any metal loading.

5. Gd doping leads to the formation of extrinsic oxygen vacancies. This may increase the oxygen ionic conductivity of the doped ceria and thus increase the CO oxidation activity of the doped ceria-supported copper oxide catalysts as well as the doped ceria material.

References

[1] S.J. Tauster, S.C. Fung and R.L. Garten, J. Am. Chem. Soc. 100 (1978) 170.
[2] S.J. Tauster and S.C. Fung, J. Catal. 55 (1978) 29.
[3] R. Burch and A.R. Flambard, J. Catal. 78 (1982) 389.
[4] W.P. Dow and T.J. Huang, J. Catal. 147 (1994) 322.
[5] D.H. Tsai and T.J. Huang, Appl. Catal. A 223 (2002) 1.
[6] J.B. Wang, H.K. Lee and T.J. Huang, Catal. Lett. (in press).
[7] M.G. Sanchez and J.L. Gazquez, J. Catal. 104 (1987) 120.
[8] W.P. Dow, Y.P. Wang and T.J. Huang, J. Catal. 160 (1996) 155.
[9] W.P. Dow and T.J. Huang, J. Catal. 160 (1996) 171.
[10] J.B. Wang, D.H. Tsai and T.J. Huang, J. Catal. 208 (2002) 370.
[11] P.L. Chen and I.W. Chen, J. Am. Ceram. Soc. 77 (1994) 2289.
[12] B.H. Chen, D. Walker, E.Y. Suard and B.A. Scott, Chem. Mater. 7 (1995) 355.
[13] H.C. Yao and Y.F. Yu, J. Catal. 86 (1984) 254.
[14] J.B. Wang, Y.L. Tai, W.P. Dow and T.J. Huang, Appl. Catal. A 218 (2001) 69.
[15] W.P. Dow, Ph.D. Thesis, National Tsing Hua University, Taiwan, 1995.
[16] M. Mogensen, T. Lindegard and U.R. Hansen, J. Electrochem. Soc. 141 (1994) 2122.
[17] L.K. Tseng and T.J. Huang, J. Chin. Inst. Chem. Engrs. 31 (2000) 493.