COMPLETE OXIDATION OF CARBON MONOXIDE AND METHANE OVER METAL-PROMOTED FLUORITE OXIDE CATALYSTS

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Abstract—Cu-Ce-O binary oxide catalysts were found to have high activity for the oxidation of CO and methane by oxygen to carbon dioxide and water as well as oxidation of CO by sulfur dioxide to carbon dioxide and elemental sulfur. The catalysts were characterized by X-ray powder diffraction, X-ray photoelectron spectroscopy (XPS), and scanning transmission electron microscopy. It was found that copper in the Cu–Ce–O system existed in the form of clusters dispersed in the cerium oxide matrix and in the form of segregated agglomerates (> 10 nm). The former are present in all catalyst compositions, while the latter increased with the copper content. The dispersed copper clusters may be stabilized by diffusion of copper ions into interstitial metal ion sites of the cerium oxide lattice forming Cu$^{+\sim}$ species in the process. Cu$^{+\sim}$ species were identified by XPS. A synergistic reaction model is proposed to explain the enhanced catalytic activity and stability. In the model, the Cu$^{+\sim}$ species on the copper cluster provide surface sites for CO adsorption and the cerium oxide provides the oxygen source. The adsorbed CO reacts with oxygen at the interface of the two materials.

1. INTRODUCTION
The interaction between metal particles and oxide support has been a fascinating catalysis subject (Bell, 1987; Stevenson et al., 1987), because many commercially important catalysts consist of small metal particles dispersed on inorganic oxide surfaces. The concepts of the strong metal-support interaction (SMSI) (Tauster et al., 1981; Baker et al., 1986) and catalysis at the interface between the metal-support (Burch and Flamand, 1982; Bell, 1987) were developed along with these studies. Although the understanding of how and why the metal-support interactions influence catalytic properties is still limited, viewing the oxide support not simply as an inert carrier has indeed provided much insight in new catalyst design. Frost (1988) predicted the existence and properties of new methanol synthesis catalysts by using the minute Schottky junction theory at the interface between metals and oxides. CO oxidation catalysts at low temperatures (below room temperature) were invented by combining precious metals (Pt, Pd) with SnO$_2$ (Sheintuch et al., 1989; Boulaouhous et al., 1990; Schryer et al., 1991) or gold with metal oxides such as α-Fe$_2$O$_3$ (Haruta et al., 1993). In both examples, the individual components alone showed low or no catalytic activity. Previous studies of the strong metal-support interaction mainly focused on precious metals (Rh, Pt, Pd, etc.). Precious metal–TiO$_2$ (Baker et al., 1986) and precious metal–CeO$_2$ (Cru, 1991) have been two classical model systems in hydrocarbon reactions and environmental catalysis, respectively. Our previous studies (Liu et al., 1994a,b) of non-precious metal–fluorite oxide catalyst systems for carbon monoxide oxidation by sulfur dioxide and oxygen as well as for the complete oxidation of methane by oxygen have indicated the presence of a synergistic effect between these two kinds of materials on the catalyst activity and stability. In this work Cu–Ce–O was chosen as a model system and catalyst activity evaluation was combined with characterization to elucidate the "strong interaction" and its effect on catalytic properties.

2. EXPERIMENTAL
2.1. Catalyst preparation and characterization
The bulk composite catalysts were prepared by coprecipitating aqueous salt solutions of the metals with ammonium carbonate or sodium carbonate. The supported catalysts were prepared by excess solution impregnation using aqueous salt solutions of the metals. Unless specifically noted, the catalysts were prepared by 4 h calcination in air at 923 K. Bulk CuO and CeO$_2$ were prepared by thermal decomposition of copper carbonate and cerium acetate (99.9%), respectively. The detailed catalyst preparation procedure was given in Liu et al. (1994b). Nano copper oxide powder was synthesized by copper vapor deposition and controlled oxidation (Tschoepe et al., 1994).
mixture of bulk cerium oxide and copper oxides was prepared by mixing the CuO and CeO$_2$ powders with water and drying the paste for 1 h at 573 K. The mixture of nano CuO and cerium oxide was prepared by mixing nano CuO, CeO$_2$, and water for 10 min in an ultrasonic water bath and following the previous drying procedure. The cerium precursor used for coprecipitation was cerium nitrate (99%) containing 4.5 at% lanthanum (Aldrich). Therefore, the cerium from this precursor is designated as Ce(La) throughout the paper. It is noted that “at %” in this paper is the atomic ratio of a metal ion to the total metal ions in the catalyst × 100%.

The catalyst characterization was performed by nitrogen adsorption/desorption on a Micromeritics ASAP 2000 apparatus for BET surface area and pore size measurement and by X-ray powder diffraction (XRD) on a Rigaku X-ray diffractometer for crystalline phase identification. The catalyst microstructure was studied by a state-of-the-art Vacuum Generators HB603 scanning transmission electron microscope (STEM) equipped with an X-ray microanalytical probe of 0.14 nm optimum resolution. For STEM analysis, the catalyst powder was dispersed on a nickel grid coated by a carbon film. The elemental mapping was conducted with the X-ray probe on the basis of a 128 × 128 data matrix. The catalyst surface was analyzed by X-ray photoelectron spectroscopy (XPS) with a Perkin Elmer 5100 system. For XPS analysis, the catalyst powder was mounted on a tantalum foil and placed into the vacuum chamber without any pretreatment. Magnesium X-ray source was used with power setting of 15 kV and 20 mA. The binding energy was adjusted to the Cls peak at 284.6 eV which existed in all measurements as an impurity.

2.2. Apparatus and procedure

The reactor was a 0.6 cm ID × 50 cm long quartz tube heated by a Lindberg furnace. The reaction temperature was monitored by a quartz-sheathed K-type thermocouple placed at the top of the packed catalyst bed. Reacting gases (CO, CH$_4$, SO$_2$) were all certified calibration gas mixtures balanced by helium (from Matheson). Air and helium (from AIRCO) were used as oxidizing gas and diluting medium, respectively. The gas streams were measured with mass flow controllers and mixed prior to the reactor inlet. The resulting gas mixture without further purification flowed downward through the packed bed. Gas composition in the product stream was analyzed by a HP5880A gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). In catalyst activity tests, the catalyst loading was typically 0.15 g and the gas flow rate was set at 100 scm, which results in a contact time of 0.09 s g/cm$^3$ and space velocity of ~40,000 v/v/h for the Cu–Ce–O catalyst (~25,000 v/v/h for the CuO, CuO/Al$_2$O$_3$). The activity was measured under steady-state conditions. For reaction rate measurement, the catalyst was diluted with silicon carbide by a weight ratio varied from 4 to 10 and the reactor was operated in differential mode with the conversion not exceeding 10%. CO and methane oxidation rates were measured at temperatures from 313 to 573 K and from 673 to 823 K, respectively, with the partial pressure of the reacting gas in the range of 100 to 7000 Pa.

3. RESULTS

3.1. CO oxidation

Figure 1 shows light-off curves of CO oxidation over various copper-containing catalysts as well as cerium oxide. The copper ion-exchanged zeolite, 3.2 at% Cu–ZSM-5, showed the lowest activity among the catalysts tested, although the same material is a very active catalyst for NO decomposition (Zhang et al., 1995). CO conversion on this catalyst was only 0.08 at 523 K. CeO$_2$ or Ce(La)O$_2$ powder had low activity under the same conditions as shown in Fig. 1. The 15 at% CuO/γ-Al$_2$O$_3$ catalyst prepared in this work showed higher activity than the Cu-ZSM-5 with 0.5 conversion at 503 K. Copper oxide is known as an active oxidation catalyst. In this work, bulk CuO prepared by decomposition of copper carbonate showed higher activity than the Cu-ZSM-5 and CuO/γ-Al$_2$O$_3$ catalysts. The light-off temperature (0.5 conversion) on the bulk CuO was 420 K. However, when the CuO powder was mixed with the CeO$_2$ powder in the atomic ratio of 15:85 by the use of a small amount of water and drying for 1 h at 573 K, the CuO light-off curve was shifted to a lower temperature by about 60 K. The coprecipitated Cu$_{0.15}$Ce(La)$_{0.85}$O$_2$ catalysts showed a little higher activity than the mixture of CuO and CeO$_2$. It is noted that the light-off curve for the CuO catalyst did not shift to low temperatures by increasing the contact time.

Figure 2 shows light-off curves of nano CuO catalysts. The 23 mg nano CuO diluted by 127 mg inert SiC particles had similar activity to the bulk CuO at low conversion (< 0.5), but the conversion leveled off slowly with increasing temperature. The activity was substantially enhanced by mixing 12 mg nano CuO with 138 mg CeO$_2$ (15 at% Cu) and the light-off temperature (0.5 conversion) decreased from 430 to 350 K. Figure 2 also includes the light-off curves over the Cu$_{0.15}$Ce(La)$_{0.85}$O$_2$ and impregnated 15 at% CuO/CeO$_2$ catalysts. The three 15 at% Cu catalysts in Fig. 2 showed the same activity independent of preparation method.

The Cu ions in the Cu-ZSM-5 catalyst are specifically associated with framework Al and well dispersed (Zhang et al., 1995). The present results indicate that neither dispersing copper at atomic level nor decreasing the CuO crystal sizes improved the copper catalyst activity for CO oxidation. The activity of copper catalyst is a strong function of the support material. The combination of copper with cerium oxide showed significant activity enhancement. Such an enhancement was observed with Cu–Ce–O catalysts prepared by different methods and cannot be explained on the basis of high copper surface area or contact time. The present Cu–Ce–O catalyst shows...
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Fig. 1. Light-off curves for CO oxidation on Cu-based catalysts (150 mg catalyst loading; 100 sccm, 2% CO, 16% O₂). (■) Cuₓ₀.₃₆Ceₓ₀.₈₅Oₓ, 30 m²/g; (●) 15 at% CuO + CeO₂, 18.6 m²/g; (▲) bulk CuO, 1.64 m²/g; (●) 15 at% CuO/Al₂O₃, 137 m²/g; (○) 3.4 at% Cu-ZSM5, 400 m²/g; (△) CeO₂, 24 m²/g.

lower light-off temperatures than alumina-supported precious metal (Pt, Pd, Rh) catalysts and higher activity than most of the base metal catalysts reported in the literature.

Since the coprecipitated Cuₓ₀.₃₆Ceₓ₀.₈₅Oₓ catalyst showed high activity, we prepared a series of Cu-Ce(La)-O catalysts by the coprecipitation method. The test results are shown in Fig. 3. The catalytic activity increased with the copper content reaching a plateau at c. 15 at%. But, heating the Cuₓ₀.₃₆Ceₓ₀.₈₅Oₓ catalyst for 3 h in flowing air at 1133 K shifted the light-off curve to low temperatures. Apparently, low copper-containing catalysts may need a high temperature activation step. Figure 4 shows the

Fig. 2. Light-off curves for CO oxidation on 15 at% Cu-containing Cu-Ce-O and nano-CuO catalysts (150 mg catalyst loading; 100 sccm, 2% CO, 16% O₂). (▲) Cuₓ₀.₃₆Ceₓ₀.₈₅Oₓ, 30 m²/g; (●) 15 at% CuO/Al₂O₃, 22.4 m²/g; (○) 15 at% nano-CuO + CeO₂, 17.6 m²/g; (■) nano-CuO, 23 mg diluted by 127 mg SiC powder.
effect of hydrogen reduction of the Cu–Ce(La)–O catalyst on its catalytic activity. The light-off curve on the fresh Cu$_{0.15}$Ce(La)$_{0.85}$O catalyst is also included. This was obtained with 0.04 g catalyst loading, that is, about four times less than the regular amount (0.15 g), and a reaction gas mixture consisting of 0.3% CO and 0.3% O$_2$ (2% CO and 16% O$_2$ for the typical test) to examine the effects of contact time and CO concentration on the light-off behavior of the Cu–Ce–O catalyst. Compared to the corresponding lines in Fig. 2, this light-off was shifted to the high temperature at high conversion by c.20 K, but the overall light-off behavior was similar, for example, 95% CO conversion was still realized at c.373 K. This result indicates that the low light-off temperature of the Cu–Ce–O catalyst is determined by its intrinsic catalytic properties. The Cu$_{0.15}$Ce(La)$_{0.85}$O catalyst activity was slightly decreased after reduction for 2 h in 25% H$_2$/He at 573 K, and significantly decreased after reduction for 1 h at 873 K. Hysteresis effects on the
oxidation of CO and methane over catalysts

3.2. Methane oxidation

Figure 5 shows the light-off curves of methane oxidation over various Cu–Ce–O catalysts at a space velocity of 45,000/h (STP). Uncombined CeO$_2$ showed the lowest activity, while the 4.5 at% La-doped CeO$_2$, Ce(La)O$_2$, showed much higher activity than CeO$_2$. The light-off curve was further shifted to lower temperatures by the addition of Cu into Ce(La)O$_2$. The Cu$_{0.15}$Ce(La)$_{0.85}$O$_2$ catalyst showed higher activity than the other Cu–Ce(La)–O catalysts containing 8 at% Cu and 50 at% Cu. Methane conversion of 50% and 95% over the Cu$_{0.15}$Ce(La)$_{0.85}$O$_2$ catalyst occurred at 723 K and 803 K, respectively. No partial oxidation products, such as CO and H$_2$, were found with the Cu–Ce(La)–O catalyst even under fuel-rich reaction conditions. Methane oxidation over the 15 at% CuO/Al$_2$O$_3$ catalyst is included in Fig. 5 for comparison. The CuO/Al$_2$O$_3$ catalyst showed comparable activity to the 8 at% and 50 at% Cu catalysts. It is noted that light-off curves in Fig. 5 were a function of catalyst surface area or contact time. The light-off curve will shift to low temperatures if the contact time is increased.

3.3. Kinetics of CO and methane oxidation

The reaction rate for CO or methane oxidation was found to increase monotonically with the partial pressure of the fuel. This behavior is intrinsically different from the precious metal catalysts for which a maximum in the rate exists with the partial pressure. The experimental data for both CO and methane oxidation were best fitted by the following equation:

$$ R_{CO} = \frac{k_i \times K_i \times P_{CO}^m}{1 + K_i \times P_{CO}} $$

(1)

$$ k_i = A \exp\left(-\frac{E_i}{RT}\right) $$

(2)

$$ K_i = K \exp\left(\frac{Q}{RT}\right) $$

(3)

where the constants, $k_i$ and $K_i$, are expressed in Arrhenius form and shown in Fig. 6, and $r$ denotes the fuel gas species (CO or CH$_4$). The results are summarized in Table 1.

3.4. Oxidation of CO by sulfur dioxide and water vapor

Oxidation of CO by stoichiometric amounts of SO$_2$([CO]/[SO$_2$] = 2) to produce elemental sulfur has potential application to elemental sulfur recovery from dilute SO$_2$-containing industrial streams. In contrast to the CO and methane oxidation, a pronounced hysteresis behavior was found on most Cu–Ce–O catalysts in CO oxidation by sulfur dioxide (Liu et al., 1994b). Since an undesirable reaction, $S + CO \rightarrow COS$, can occur in this process, the selectivity to elemental sulfur over COS is another criterion in addition to activity to rank the catalyst performance. Thus, Table 2 lists the light-off temperatures with SO$_2$ conversion and sulfur yield measured under steady-state conditions during temperature fall-off. Because high temperatures always favor the present reaction, only the data at lower temperatures were used for comparison. The data in Table 2 show that copper significantly

![Fig. 5. Light-off curves of methane oxidation over the Cu–Ce–O and 15 at% CuO/Al$_2$O$_3$ catalysts (150 mg catalyst loading, 100 sccm, 2% CH$_4$, 16% O$_2$). (V) Cu$_{0.15}$Ce(La)$_{0.85}$O$_2$, 30 m$^2$/g; (▲) Cu$_{0.09}$Ce(La)$_{0.91}$O$_2$, 43.2 m$^2$/g; (●) Cu$_{0.5}$Ce-(La)$_{0.5}$O$_2$, 27.1 m$^2$/g; (O) at 15 at% CuO/Al$_2$O$_3$, 137 m$^2$/g; (●) Ce(La)O$_2$, 27 m$^2$/g; (□) CeO$_2$, 24 m$^2$/g.](image-url)
Fig. 6. Arrhenius plots of constants $k_s$ and $K_r$ for CO and methane oxidation over Cu–Ce(La)–O catalysts. Closed symbols for ln($K_r$) and the open for ln($k_s$). (●) methane oxidation, Cu$_{0.15}$Ce(La)$_{0.85}$O$_2$; (■) CO oxidation, Cu$_{0.15}$Ce(La)$_{0.85}$O$_2$; (▽) CO oxidation, Cu$_{0.05}$Ce(La)$_{0.95}$O$_2$; (▲) CO oxidation, Cu$_{0.05}$Ce(La)$_{0.95}$O$_2$, further heated for 3 h in air at 1133 K.

Table 1. Oxidation kinetics over the Cu–Ce(La)–O catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>n</th>
<th>A</th>
<th>$E_a$ (kJ/mole)</th>
<th>$Q$ (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO oxidation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{0.15}$Ce(La)$</em>{0.85}$O$_2$</td>
<td>0.077 ± 0.026</td>
<td>$1.44 \times 10^{10}$</td>
<td>78.0</td>
<td>$6.47 \times 10^2$</td>
</tr>
<tr>
<td>Cu$<em>{0.05}$Ce(La)$</em>{0.95}$O$_2$, fresh†</td>
<td>-0.086 ± 0.019</td>
<td>$3.63 \times 10^6$</td>
<td>72.7</td>
<td>$6.82 \times 10^3$</td>
</tr>
<tr>
<td>+ heated 3 h in air at 1133 K</td>
<td>0.116 ± 0.023</td>
<td>$6.76 \times 10^{10}$</td>
<td>87.3</td>
<td>$2.50 \times 10^5$</td>
</tr>
<tr>
<td>Methane oxidation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{0.15}$Ce(La)$</em>{0.85}$O$_2$</td>
<td>0.176 ± 0.025</td>
<td>$6.98 \times 10^5$</td>
<td>93.4</td>
<td>$3.46 \times 10^5$</td>
</tr>
</tbody>
</table>

†Prepared by standard calcination procedure: 4 h in air at 923 K.
‡Prepared by 4 h heating in N$_2$ at 873 K.

Table 2. Catalyst activity and selectivity for CO oxidation by sulfur dioxide†

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Light-off temperature, $T_{90%}(K)$</th>
<th>Y-sulfur/X-SO$_2$§</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>743 K</td>
</tr>
<tr>
<td>Ce(La)$_2$O$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{0.05}$Ce(La)$</em>{0.95}$O$_2$</td>
<td>883</td>
<td>0.96/0.20</td>
</tr>
<tr>
<td>Cu$<em>{0.15}$Ce(La)$</em>{0.85}$(La)O$_{1-x}$</td>
<td>773</td>
<td>0.97/1.00</td>
</tr>
<tr>
<td>Cu$<em>{0.25}$Ce(La)$</em>{0.75}$(La)O$_{1-x}$</td>
<td>773</td>
<td>0.97/0.99</td>
</tr>
<tr>
<td>15 at% CuO/Cr$_2$O$_3$</td>
<td>773</td>
<td>0.93/0.97</td>
</tr>
<tr>
<td>15 at% CuO/γ-Al$_2$O$_3$§</td>
<td>823</td>
<td>0.84/0.92</td>
</tr>
</tbody>
</table>

Reactions include 2CO + SO$_2$ → CO$_2$ + 1/2S, and S + CO → COS. Reacting gas mixture consists of 1% SO$_2$, 2% CO, and balance helium.
†Reaction temperature at which more than 90% conversion occurred.
§Y-sulfur and X-SO$_2$ are elemental sulfur yield, [S]/[SO$_2$]$_o$, and SO$_2$ conversion, ([SO$_2$]$_o$-[SO$_2$])/[SO$_2$]$_o$, respectively, where [SO$_2$]$_o$ denotes inlet sulfur dioxide concentration.
¶Prepared in-house by wet impregnation from aqueous solution of copper nitrate on γ-Al$_2$O$_3$(La Roche), dried and calcined at 923 K for 4 h.
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Table 3. Conversion of CO to CO₂ over the Cu₀.₁₅Ce(La)₀.₇₅O₂ catalyst in the water-gas shift reaction

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Cu₀.₁₅Ce(La)₀.₇₅O₂</th>
<th>CeO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16% H₂O 9% H₂O</td>
<td>9% H₂O</td>
</tr>
<tr>
<td>489</td>
<td>0.61</td>
<td>—</td>
</tr>
<tr>
<td>588</td>
<td>0.94 0.34</td>
<td>—</td>
</tr>
<tr>
<td>635</td>
<td>0.97 0.591</td>
<td>—</td>
</tr>
<tr>
<td>731</td>
<td>0.985 0.744 0.04</td>
<td>—</td>
</tr>
</tbody>
</table>

*Reaction conditions: 100 sccm He + CO + H₂O containing 2% CO, 150 mg catalyst loading.*

promoted the cerium oxide catalyst activity by lowering the light-off temperature from 883 K to 773 K and extending the fall-off temperature below 773 K. The copper content showed little effect on catalytic activity, but, there was a tendency for the sulfur yield to decrease as the copper content increased. The CuO/-Al₂O₃ catalyst prepared in this work showed overall inferior performance to the Cu–Ce(La)O catalyst in terms of activity, selectivity and stability, although it had high surface area.

It is known that copper is not a catalyst for the water-gas shift (WGS) reaction. Cerium oxide is believed to have some promotion effect on the WGS reaction in the automotive three way catalyst. However, the test data in Table 3 show small CO conversion on the Ce(La)O₂ at low temperatures. Similar to the Cu–Zn–O system, the Cu₀.₁₅Ce(La)₀.₇₅O₂ is an active catalyst for the WGS reaction. For example, the CO conversion was only 0.04 on the Ce(La)O₂ at 731 K but 0.744 on the Cu₀.₁₅Ce(La)₀.₇₅O₂ catalyst. Increasing the water vapor content favored the WGS reaction.

3.5. Catalyst characterization

3.5.1. XRD and STEM analyses. Figure 7 shows the XRD pattern of the Cu–Ce–O catalysts prepared by coprecipitation. The major peaks were due to the CeO₂ crystal phase. CuO phase appeared in smaller peaks and increased with the copper content. No CuO peak could be seen for the catalyst containing less than 15 at% Cu. Figure 8 shows the XRD pattern of various 15 at% Cu-containing catalysts. Since the relative intensity of the CuO peak was so small compared to that of the CeO₂ peak, only the regions of copper-related crystal phase are given for easy comparison. The relative intensity of a peak can be referred to the baseline. The bulk Cu₀.₁₅Ce(La)₀.₇₅O₂ catalyst had lower CuO peak intensity than the impregnated and mixed ones. Metallic copper peaks appeared after the catalyst was reduced by 25% H₂/He, while the CuO...
peaks disappeared. No Cu$_2$O crystal phase was detected.

Copper in the Cu–Ce–O system could not be distinguished from cerium in electron microscopy images because of the lower copper atomic weight and content relative to cerium. STEM proved to be a powerful tool for the Cu–Ce–O catalyst characterization. The elemental maps obtained with the STEM X-ray probe on a 128 × 128 data matrix are shown in Fig. 9(a)–(g). Extensive mapping on the Cu$_{0.15}$Ce-

![Fig. 8. XRD pattern of various 15 at% Cu-containing Cu–Ce–O catalysts (50 kV, 200 mA, Cu Kα1 radiation).](image)

![Fig. 9. Elemental maps of Cu–Ce–O catalysts acquired by STEM X-ray probe on a 128 × 128 data matrix. (a) Cu$_{0.15}$CeLa$_{0.85}$O$_x$ (600kX) – contd.](image)
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Fig. 9 - contd. (b) Cu$_{0.5}$Ce(La)$_{0.5}$O$_x$(130 K ×).

Fig. 9 - contd. (c) Cu$_{0.5}$Ce(La)$_{0.5}$O$_x$(330 k ×).

(La)$_{0.85}$O$_x$ catalyst found that cerium as the major component comprised a continuous phase, while copper existed in the form of big agglomerates (> 10 nm) and fine particles or clusters (~ nm). Figure 9(a) is a typical elemental map of the Cu$_{0.15}$Ce(La)$_{0.85}$O$_x$ catalyst comprising the image on the upper left corner, oxygen map on the upper right corner, cerium map on the lower left corner, and copper map on the lower right corner. The Cu map consisted of a big CuO particle (17 nm) and a number of tiny copper spots distributed in the cerium oxide matrix. These copper domains could not be definitely differentiated from the solid solution as distinguishable fine copper particles due to the lighter copper atomic weight relative to cerium and the instrumental limitation itself. Few fine copper oxide crystals (nm) were found in the Cu$_{0.15}$Ce(La)$_{0.85}$O$_x$ catalyst by high-resolution transmission electron microscopy. Taking into account the insolubility of copper oxide in cerium oxide and further characterization evidence from other Cu–Ce–O catalysts as given below, these tiny copper domains are attributed to copper clusters invisible by XRD. The observations for the 15% Cu-containing CuOx/CeO$_2$ and CuO + CeO$_2$ mixture catalysts were similar to the
Fig. 9 – contd. (d) Cu_{0.01}Ce(La)_{0.99}O_{2} prepared by heating for 4 h in N\textsubscript{2} at 873 K (330 K \times 3). 

Fig. 9 – contd. (e) Cu_{0.01}Ce(La)_{0.99}O_{2} further heated for 3 h in flowing air at 1133 K (330 K \times 3).

Cu_{0.15}Ce(La)_{0.85}O_{2} catalyst. Qualitatively, more segregated bulk CuO particles were found in the CuO + CeO\textsubscript{2} catalyst.

Figures 9(b) and (c) show the elemental maps of the Cu_{0.15}Ce(La)_{0.85}O_{2} catalyst. A large number of copper agglomerates were observed with this higher copper-containing material. In addition, these big CuO particles were typically covered by smaller cerium oxide particles. This finding is illustrated by Fig. 9(b) in which a big CuO agglomerate (c. 300 nm) was almost fully covered by the CeO\textsubscript{2} particles. But, when we look at a group of CeO\textsubscript{2} particles not associated with bulk CuO, a number of copper clusters are still dispersed in the cerium oxide matrix particles shown in Fig. 9(c). It is noted that the existence of these copper clusters was confirmed by electron-excited X-ray emission spectra. These observations generally agree with the XRD results. The bigger the CuO peak in XRD, the higher the number of big copper particles found by STEM. But, the fine copper particles or clusters, which were invisible by XRD, were revealed by STEM X-ray mapping.
Figure 9(d) shows a typical map of the fresh Cu$_{0.01}$Ce(La)$_{0.99}$O$_x$ catalyst prepared by 4 h calcination at 873 K in N$_2$. The Cu distribution pattern was closely correlated with that of cerium and no copper segregation was observed, which strongly suggests the uniform copper dispersion and formation of solid solution. After the catalyst was heated for 3 h in flowing air at 1113 K, copper segregation and formation of copper clusters were observed. Figure 9(e) shows that the elemental map is now similar to Fig. 9(a) for the Cu$_{0.15}$Ce(La)$_{0.85}$O$_x$ catalyst and Fig. 9(c) for the Cu$_{0.5}$Ce(La)$_{0.5}$O$_x$ catalyst except for the absence of bulk CuO particles.

Copper clusters in the Cu$_{0.15}$Ce(La)$_{0.85}$O$_x$ catalyst grew to form metallic copper particles after the catalyst was reduced in 25% H$_2$/He. Figure 9(f) shows the elemental map after 2 h reduction at 573 K. The metallic copper particles can be identified by the absence of associated oxygen in the oxygen map. A large number of copper particles were found in the...
reduced catalyst, that was consistent with the strong XRD peaks of metallic copper in Fig. 8. In addition to these bulk copper particles, a significant number of copper clusters remained dispersed in the cerium oxide matrix. However, the population of the copper clusters significantly diminished after that catalyst was reduced for 1 h at 873 K as shown in Fig. 9(g). In separate reduction studies of the Cu–Ce–O system by hydrogen conducted in a TGA apparatus, the complete reduction of copper in the Cu–Ce–O system to metallic copper in 25% H₂/He took only a few minutes at 873 K. It is known that the coalescence rate of metallic copper particles grows exponentially with temperature. By placing the X-ray probe on different spots of a metallic copper particle adjacent to the cerium oxide matrix, such as the center, edge, near edge, etc., oxygen was identified on the metallic copper particle though its amount was small relative to copper. There were no oxygen-free metallic copper particles even under the 10⁻¹¹ torr vacuum of the STEM apparatus.

3.5.2. XPS studies. Figure 10 shows the Cu2p XP spectra of the Cu–Ce(La)–O composite catalysts. No Cu2p3/2 shake-up peak was observed with the Cu₉₀₁Ce₁La₀9O₉ catalyst and small shake-up peak was found with the Cu₀₁₅Ce₁La₀₈₅O₉ and Cu₀₃Ce₁La₀₇O₉ catalysts. The shake-up peak and higher Cu2p3/2 binding energy are two major XPS characteristics of Cu²⁺ in bulk CuO, while the lower Cu2p3/2 binding energy and absence of a shake-up peak are characteristic of reduced copper oxide species (Cu⁺, Cu₂O) (Wagner et al., 1978). The Cu2p3/2 peaks for the Cu₀₁Ce₁La₀₉₉O₉ catalyst were deconvoluted into two components: one at 933.1 eV and another at 930.0 eV. The Cu2p3/2 peaks for the Cu₁₅Ce₁La₀₈₅O₉ and Cu₀₃Ce₁La₀₇O₉ catalysts were deconvoluted into two main components: one at 934.0 eV and another at 933.1 eV. Figure 11 shows the kinetic energy spectra of the Auger L₃VV electron for the corresponding XP spectra in Fig. 10. The Auger peak can be roughly separated into two components: one at 918.2 eV and another at 915.7 eV. Taking into account these results and literature studies (Wagner et al., 1978; Jin et al., 1987; Wright et al., 1992; Shpiro et al., 1994) the XPS Cu2p3/2 peak component at 933.1 eV was assigned to Cu¹¹ species and the component at 934.0 eV was assigned to CuO. Correspondingly, the L₃VV Auger peaks at 918.2 eV and 915.7 eV are due to CuO and Cu⁺⁺ species, respectively.

It is seen from the XP spectra that the CuO component increased with the copper content. The Cu2p3/2 peak component at 930.0 eV for the Cu₀₁Ce₁La₀₉₉O₉ catalyst was difficult to be assigned since no copper species of such a low binding energy have been reported in the literature. According to an EPR study of the Cu–Ce–O mixed oxide (Cu/Ce = 0.01) by Abou Kais et al. (1992) and similar studies of Cu–Th–O mixed oxides by Bechara et al. (1990a,b), isolated monomeric copper(II) species and copper ion pairs exist in the cerium oxide. The isolated copper ions in octahedral sites with a tetragonal distortion were the precursors of copper ion pairs in cerium oxide. Therefore, the unknown component at 930.1 eV is tentatively assigned to the isolated...
monomeric copper(II) ions in cerium oxide. Figure 10 shows that the fraction of the Cu$^{+1}$ species in the XP spectra of the Cu$_{0.01}$Ce(La)$_{0.99}$O$_{x}$ catalyst increased after the catalyst was heated in air, while the 930.0 eV component decreased. This suggests that the isolated copper(II) ions migrated together to form copper ion pairs or clusters with the Cu$^{+1}$ species stabilized in the process. Figures 12 and 13 show the XP spectra and Auger L$_{3}$VV spectra of various 15 at% Cu-containing

![Figure 11. Kinetic energy spectra of Auger L$_{3}$VV electron of copper in Cu–Ce(La)–O catalysts.](image)

![Figure 12. Cu$_{2p}$ XP spectra of CuO and hydrogen-reduced Cu$_{0.15}$Ce(La)$_{0.85}$O$_{x}$ catalysts (Mg, 15 kV, 300 W).](image)
catalysts together with the bulk CuO respectively. The bulk CuO shows a clear XPS shake-up in Fig. 12 and a sharp Auger L\textsubscript{3}VV peak at 918.2 eV in Fig. 13. The hydrogen-reduced Cu\textsubscript{0.15}Ce(La)\textsubscript{0.85}O\textsubscript{x} catalysts had a Cu\textsubscript{2p3/2} peak position mainly at 933.0 eV with a small shake-up peak. The Auger L\textsubscript{3}VV line of metallic copper is generally the same or close to CuO. The broad L\textsubscript{3}VV peaks for the hydrogen-reduced Cu\textsubscript{0.15}Ce(La)\textsubscript{0.85}O\textsubscript{x} in Fig. 13 may be composed of all copper species, CuO, Cu\textsuperscript{0}, and Cu\textsuperscript{+}. This indicates that the metallic copper surface was partially oxidized when it was exposed to air at room temperature, as observed by STEM.

Surface compositions analyzed by XPS for the catalysts tested in this work are summarized in Table 4. For the Cu–Ce–O catalysts containing less than 15 at% Cu, the surface appeared to be enriched in copper and surface copper content increased with the bulk content. Calcining the Cu\textsubscript{0.05}Ce(La)\textsubscript{0.95}O\textsubscript{x} catalyst in air drove more copper to the surface. These results indicate the immiscibility of copper and cerium oxide. However, reduction of the Cu\textsubscript{0.15}Ce(La)\textsubscript{0.85}O\textsubscript{x} catalyst by hydrogen did not increase the surface copper content, although copper was certainly segregated from the bulk. This is explained based on the STEM analyses that reduction did not result in better surface compositions.

![Fig. 13. Kinetic energy spectra of Auger L\textsubscript{3}VV electron of copper in CuO and hydrogen-reduced Cu\textsubscript{0.15}Ce(La)\textsubscript{0.85}O\textsubscript{x} catalysts.](image)

**Table 4. CO oxidation activity and surface composition of Cu–Ce–O catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m\textsuperscript{2}/g)</th>
<th>Light-off, (T_{50%}(\text{K}))</th>
<th>Surface composition (%)\textdagger\textdagger\textcircled{1}</th>
<th>Cu</th>
<th>Ce</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu\textsubscript{0.05}Ce(La)\textsubscript{0.95}O\textsubscript{x}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated 3 h in air at 1133 K</td>
<td>57.0</td>
<td>423</td>
<td>5.0</td>
<td>89.0</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>Cu\textsubscript{0.05}Ce(La)\textsubscript{0.95}O\textsubscript{x}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 h in 25% H\textsubscript{2}/He at 573 K</td>
<td>25.7</td>
<td>355</td>
<td>18.7</td>
<td>75.7</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>1 h in 25% H\textsubscript{2}He at 873 K</td>
<td>22.1</td>
<td>405</td>
<td>15.5</td>
<td>78.1</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>15 at% CuOx/CoO</td>
<td>22.4</td>
<td>353</td>
<td>16.6</td>
<td>83.4</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>15 at% CuO + CeO\textsubscript{2}</td>
<td>18.6</td>
<td>360</td>
<td>9.2</td>
<td>90.8</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Cu\textsubscript{0.25}Ce(La)\textsubscript{0.75}O\textsubscript{x}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>27.8</td>
<td>352</td>
<td>18.7</td>
<td>75.4</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>Cu\textsubscript{0.25}Ce(La)\textsubscript{0.75}O\textsubscript{x}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>27.1</td>
<td>340</td>
<td>18.9</td>
<td>75.3</td>
<td>5.8</td>
<td></td>
</tr>
</tbody>
</table>

\textdagger Determined by XPS with a standard deviation of ±1.5%.

\textdagger\textdagger Prepared by 4 h calcination in N\textsubscript{2} at 873 K.
copper dispersion because of the formation of bulk metallic copper particles. The variation of surface copper content with the preparation method for the 15 at% Cu catalysts and low copper surface content for the catalysts containing a high amount of copper are also explained on the basis of the STEM results. Three forms of copper, namely, ions, clusters, and bulk CuO particles, exist in a Cu–Ce–O system. The bulk CuO particles were typically covered by cerium oxide particles. Increasing bulk copper content above c. 15 at% Cu only enhanced the formation of bulk CuO particles as observed by the strong XRD peaks of CuO. Coprecipitated 15 at% Cu catalyst gave rise to better copper dispersion than the other methods under the same calcination condition. The observation that CuO particles were covered by fine cerium oxide particles is intriguing and the subject of future work.

4. DISCUSSION

4.1. CO oxidation

Table 4 lists the CO oxidation light-off temperatures and surface compositions of the Cu–Ce–O catalysts. There is no simple correlation between the light-off temperature with either bulk composition or surface composition, which suggests that the activity was determined by some specific catalyst properties. On the basis of the above experimental results, it is proposed that the active sites in the Cu–CeO catalyst are the copper clusters distributed in the cerium oxide matrix as shown in Fig. 14.

The copper cluster is stabilized by "strong interaction" with the cerium oxide matrix and Cu⁺ sites are also created by such an interaction. CO molecules adsorb on Cu⁺ sites of a copper cluster. The adsorbed CO reacts with the oxygen species on the cerium oxide surface at the boundary. The experimental reaction rate eq. (1) for CO and methane oxidation can be obtained by assuming a Langmuir–Hinshelwood mechanism, that is, the surface reaction is the rate-determining step. CO adsorption is described by a Langmuir equation, \( K_{\text{co}} P_{\text{co}}/(1 + K_{\text{co}} P_{\text{co}}) \). There could be a variety of surface oxygen sources as is discussed below so that the rate dependence on the partial pressure of oxygen was approximated by a power order. Therefore, \( k_s \) and \( K_s \) in the rate expression shown in eq. (1) mean the surface reaction constant and adsorption equilibrium constant, respectively. The activation energies, 78–94 kJ/mole for CO oxidation and 93.4 kJ/mole for methane oxidation, agree with literature data (Liao et al., 1982; Choi and Vannice, 1991; Dekker et al., 1992; Seiyama, 1992).

The heat of CO adsorption, 28–61 kJ/mole, is similar to CO adsorption on Cu/SiO₂ measured by Clarke et al. (1993) and Sandval and Bell (1993), while the heat of methane adsorption, 14.2 kJ/mole, is relatively small. It is known that CO adsorbs on Cu⁺ or Cu sites much stronger than on CuO (London and Bell, 1973). Therefore, one of the characteristics of the present catalyst system is the existence of the Cu⁺ surface sites for CO adsorption.

4.2. Interaction of copper and cerium oxide

How the "strong interaction" between copper clusters and cerium oxide can lead to Cu⁺ formation is now considered. Sanchez and Gazquez (1987) proposed the model of metal occupancy of surface vacancies in fluorite oxides to account for the strong interaction between metals and fluorite oxides. Dow and Huang (1994) applied the vacancy model to interpret the CO oxidation over the Cu/YSZ catalyst.

It is known that the oxygen vacancy in a fluorite oxide is a positively charged lattice site and usually capped by an outside oxygen (Gerhardt-Anderson and Nowick, 1981; Yao and Yao, 1984; Butler et al., 1988). It is difficult to energetically visualize a metal ion such as Cu²⁺ occupying a vacancy site. An interstitial model, illustrated by Fig. 15, is proposed to account for the interaction of copper and cerium oxide.

Cerium oxide has a stable fcc crystal structure from room temperature up to its melting point. In a unit cell of cerium oxide, there are eight cubes formed by oxygen atoms at the vertices, the four of them hosting Ce⁴⁺ ions in their center sites, while the other four are empty. The empty cube can host a copper ion at an interstitial cerium ion site. The electron neutrality in the unit cell containing a copper ion can be balanced by surface capping oxygen or conversion of a Ce⁴⁺ ion to Ce³⁺ ion in the presence of a Cu⁺ ion. The isolated copper ions will not be active and stable catalytic sites, because they can be capped by oxidants or are not easily accessible to the reactant. When a copper cluster exists on the cerium oxide matrix, however, many catalytic properties can be enhanced. The penetration of the copper ions into the cerium oxide lattice stabilizes the copper cluster.
Exposed copper surface becomes accessible to the reactant. In contrast to bulk copper oxide, the copper atom in such a cluster may adopt a variety of states. The Cu$^{+1}$ species on the outer surface of a copper cluster is stabilized by associating with the embedded Cu ion inside the cerium oxide. The present active and stable catalysts were prepared by calcination at 923 K in air, which suggests that the Cu$^{+1}$ species in the Cu–Ce–O system is stable under reaction conditions. In addition, the exchange of Ce$^{+4}$ to Ce$^{+3}$ ion in the cerium oxide may also be facilitated by the introduction of copper ions. The Ce$^{+3}$ itself is an active catalyst for the CO oxidation (Tschoepe et al., 1994).

The kinetic parameters in Table 1 for CO oxidation on the Cu$_{0.01}$Ce(La)$_{0.99}$O$_2$ catalyst varied considerably with the thermal treatment process. A negative order in $P_O$ was found for the fresh Cu$_{0.01}$Ce(La)$_{0.99}$O$_2$ catalyst prepared by calcination at 873 K in N$_2$. This may be due to oxygen inhibiting the CO adsorption by capping the Cu sites as predicted by the model. Since both XPS and STEM characterization suggest that a large fraction of copper in this catalyst exists as isolated ions or in a solid solution form. After the fresh Cu$_{0.01}$Ce(La)$_{0.99}$O$_2$ catalyst was further heated for 3 h in flowing air at 1133 K, the reaction order in $P_O$ changed to positive, while the pre-exponential factor of the reaction constant $K_m$ increased by four orders of magnitude and the heat of adsorption increased from 36.8 kJ/mole to 61.2 kJ/mole. This change is correlated to the increasing fraction of Cu$^{+1}$ species in the XP spectra and the evolution of the isolated ions to clusters as observed by STEM. The reduction of Cu$_{0.15}$Ce(La)$_{0.85}$O$_2$ catalyst by hydrogen converted the copper oxide to metallic form. The copper metal particles, either by surface partial oxidation or without, can also provide surface sites for chemisorption. That is why the reduced catalyst by 25% H$_2$/He at 573 K still had high activity. Loss of copper clusters to bigger copper metallic particles by hydrogen reduction at 873 K significantly decreased the catalytic activity.

Our discussion so far has stated the importance of Cu$^{+1}$ species to achieve high activity. Cu$^{+1}$ species may be formed in the mixed oxide of copper with other base metal oxides (Agudo et al., 1992; Wright et al., 1992; Shpiro et al., 1994), such as chromium oxide, cobalt and manganese oxide, etc. However, the CO oxidation activity over these oxide catalysts reported in the literature was generally much lower than the present Cu–Ce(La)–O catalyst. Therefore, participation or promotion by cerium oxide needs to be considered.

### 4.3. Role of cerium oxide in oxygen activation

Metcalfe and Sundaresan (1988) proposed the interface reaction model for CO oxidation over the Pt/YSZ catalyst and Haruta et al. (1993) applied the model to the gold/metal oxide system. In both cases, Pt or Au provides the site for CO adsorption, while the metal oxide serves as the oxygen source. The physical model depicted in Fig. 14 is similar to those cases except for the Cu$^{+1}$ sites for CO adsorption. Li et al. (1989a,b) detected superoxide species (O$_2^-$) from oxygen adsorption on cerium oxide and found that the exchange between the superoxide species and gaseous oxygen was fast at temperatures below 373 K, while no exchange between gaseous oxygen and lattice oxygen occurred at such temperatures. Li et al. (1993a) also found that the adsorbed dioxygen species was labile on the cerium oxide surface. Martin and Duprez (1993) measured the surface diffusion of oxygen on different supports and found that diffusion on cerium oxide was several hundred times higher than that on SiO$_2$ or Al$_2$O$_3$. In addition to the superoxide species, surface capping oxygen and lattice oxygen are two other oxygen species available on the cerium oxide surface. Yao and Yao (1984) found that the presence of precious metals lowered the surface capping reduction temperature. Sayle et al. (1992) simulated the CeO$_2$ crystal and suggested that surface lattice oxygen and vacancy are more active than the bulk. Li et al. (1993b) observed that methane oxidation occurred in the absence of gaseous oxygen and O$_2$ species. Fixed bed, steady-state measurements of CO and methane oxidation in this lab found that these two reactions were independent of each other, which is different from precious metal catalysts.

Taking into account these previous studies and our data, the reactions studied in this work are classified with the prevalent surface oxygen species using the physical model in Fig. 14.

\[
\text{(i) } \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \\
\text{(ii) } \text{CH}_4 \rightarrow \text{CO} + 2\text{H}_2 \\
\text{(iii) } \text{CH}_4 + \text{O-cat} \rightarrow \text{CH}_3\text{CHO} + \text{HO-ad} \\
\text{(iv) } \text{CH}_4 + \text{O-cat} \rightarrow \text{CH}_3\text{COOH} + \text{HO-ad}
\]

Superoxide species (O$_2^-$) on cerium oxide is the oxygen source for this reaction. Thus, the activity is not affected by small amounts of dopant oxides that increase the oxygen vacancies of cerium oxide. The creation of Ce$^{+3}$ species by the introduction of multivalent copper ion into its lattice is helpful for the reaction (Tschoepe et al., 1994).

\[
\text{(i) } \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \\
\text{(ii) } \text{CH}_4 + \text{O-cat} \rightarrow \text{CH}_3\text{CHO} + \text{HO-ad}
\]

Surface capping oxygen and lattice oxygen/vacancy are the oxygen sources for this reaction. The abstraction of hydrogen from adsorbed CH$_4$ to form the carbonium intermediate is thought to be the rate-determining step. Suitable surface acidic sites for hydrogen abstraction and nucleophilic sites for carbonium stabilization are essential. These properties of cerium oxide can be tuned by doping cerium oxide with alkaline and rare earth oxides in suitable amounts. Methane shows weak adsorption on the base metal oxide. The presence of the Cu$^{+1}$ species may aid methane adsorption on the Cu–Ce(La)–O catalyst.
A redox reaction mechanism on metal oxide catalysts has been proposed for the WGS reaction by Lund et al. (1985) and for the sulfur dioxide reduction by Happel et al. (1977). The creation of catalyst surface vacancy is the rate-determining step. An oxygen vacancy is created when the adsorbed CO picks up an oxygen from the cerium oxide surface, probably capping oxygen. The vacancy is then filled by an oxygen from the SO\textsubscript{2} or H\textsubscript{2}O molecule. The high oxygen vacancy mobility in cerium oxide allows diffusion of the oxygen vacancy on the surface. Li et al. (1989c,d) found that water vapor strongly inhibits the adsorption of CO on cerium oxide. Because of this inhibition effect, the catalytic activity of cerium oxide for sulfur dioxide reduction was dramatically reduced by water vapor and the WGS reaction on the cerium oxide catalyst proceeded at less than 5% conversion below 823 K. However, the Cu\textsuperscript{+1} species in the Cu–Ce–O catalyst provide surface sites for CO adsorption; hence, the very high activity of the Cu–Ce–O system for these two reactions.

5. CONCLUSION

Copper in the Cu–Ce–O composite exists in three forms: (i) isolated ions uniformly embedded in the cerium oxide matrix; (ii) clusters sparsely distributed in the cerium oxide matrix; (iii) segregated bulk CuO particles covered by smaller cerium oxide particles. The relative amounts of these three forms are strong functions of the copper content and thermal treatment. Generally, the segregated bulk CuO increases with copper content and thermal treatment temperature. But, no simple rules exist to predict the other two species. The copper clusters on the cerium oxide provide the high catalyst activity. To achieve such a catalyst structure, theoretically, only a few atomic percent of copper may be needed. A unified reaction model based on this catalyst microstructure is proposed to interpret the four reactions studied in this work. In this model, the copper clusters are stabilized through penetration of copper ions at the interfacial area into the interstitial metal sites of the cerium oxide lattice, and Cu\textsuperscript{+1} result from this "strong interaction". The Cu\textsuperscript{+1} species on the copper cluster provide surface sites for CO chemisorption and probably also for methane. The cerium oxide provides the oxygen source. The chemisorbed CO reacts with the oxygen at the interface of these two materials. The CO–O\textsubscript{2}, CO–SO\textsubscript{2}, CO–H\textsubscript{2}O, and CH\textsubscript{4}–O\textsubscript{2} reactions were classified by the participation of different surface oxygen species on cerium oxide.

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