Carbon oxidation activity of complex oxides (Part 1) — RE_2CuO_4 ($\text{RE} = \text{La-Gd}$) and $\text{RE}_2\text{Cu}_2\text{O}_5$ ($\text{RE} = \text{Dy-Yb, Y}$)—

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Effect of rare earths (RE) in the rare earth copper oxides, RE_2CuO_4 ($\text{RE} = \text{La, Pr, Nd, Sm, Gd}$) and $\text{RE}_2\text{Cu}_2\text{O}_5$ ($\text{RE} = \text{Dy, Ho, Er, Yb, Y}$), on the carbon oxidation was investigated by the DSC (differential scanning calorimetry) measurement. Orthorhombic La_2CuO_4 and tetragonal RE_2CuO_4 ($\text{RE} = \text{Pr-Sm}$) prepared at 800°C showed higher carbon oxidation activity compared with CuO processed at the same temperature, whereas activity of the orthorhombic $\text{RE}_2\text{Cu}_2\text{O}_5$ ($\text{RE} = \text{Dy-Yb, Y}$) prepared at 1000°C was lower than that of CuO processed at the same temperature.

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1. Introduction

Diesel engines emit a large amount of particulate matter (PM) which is hazardous waste for human health, though they have advantages of higher thermal efficiency and less CO_2 emission, compared with gasoline engines.

Ceramic foam and diesel particulate filter (DPF) are generally designed to remove PM from the diesel exhaust gases. However, since the modern diesel engine exhaust gases are relatively low in their temperature, well below the ignition point of PM in air, the collected PM cannot burn promptly and is accumulated on the ceramic foam and DPF to cause a serious pressure loss in the engine system, resulting in a lowering of fuel-efficiency. In order to overcome these problems, much attention has been paid to the development of catalysts which promote the combustion (oxidation) of soot (carbon) as a principal ingredient of PM at low temperature.¹⁾⁻⁸⁾ In those development, mixed metal oxides containing rare earth ions have been reported to be effective catalysts. Besides these studies, it was reported, in 2008, that the transition metal oxides, including CuO, exhibit high carbon oxidation performance.⁹⁾ Recently, the addition of CuO to CeO_2 , i.e., Cu-doped CeO_2 , has been found to decrease the combustion temperature of carbon black/soot over the CeO_2 catalyst.^{10),11)} These results stimulate us to investigate the combination of CuO and rare earth oxides except for CeO_2 toward the development of catalysts with high performance. In the present work, the carbon oxidation activity of RE_2CuO_4 ($\text{RE} = \text{La, Pr, Nd, Sm and Gd}$) and $\text{RE}_2\text{Cu}_2\text{O}_5$ ($\text{RE} = \text{Dy, Ho, Er, Yb and Y}$) was examined as an opening research on the catalytic activity of RE-Cu-O systems.

2. Experimental procedure

In preparation of the RE_2CuO_4 and $\text{RE}_2\text{Cu}_2\text{O}_5$ powders, CuO (Wako Pure Chemical Industries, Ltd., Reagent grade) and rare earth oxide [RE_2O_3 ($\text{RE} = \text{La, Nd, Sm, Gd, Dy, Ho, Er, Yb and Y}$)

and Pr_6O_{11} : Shin-Etsu Chemical Co., Ltd., 99.9%-grade] were mixed in an ion-exchanged water using a ball-mill. The mixture was dried and calcined at 600, 700, 800, 900, 1000, 1100 and 1200°C in air for 2 h. The resulting powders were again ball-milled into finer powders and dried. Powder samples thus obtained were characterized by the measurement of powder X-ray diffraction (XRD, Rigaku MiniFlex) using $\text{Cu K}\alpha$ radiation in the 2θ range of 10 to 70°. Three point BET method by the N_2 gas adsorption (Quantachrome NOVA3200) was applied for the determination of specific surface area after each powder was deaerated at 200°C. Powder sample and carbon black (Tokai Carbon Co., Ltd., #8500/F) as a model soot were well mixed in the powder/carbon weight ratio of 19:1, and the mixture was subjected to the evaluation of carbon oxidation activity. The oxidation (combustion) experiments were carried out by heating the mixture (10 mg) from room temperature to 700°C at $10^\circ\text{C min}^{-1}$ in a 20 ml min^{-1} air flow, using the differential scanning calorimeter (DSC, Rigaku DSC8230) and the thermo-gravimetric and differential thermal analyzer (TG-DTA, Rigaku TG8120).

3. Results and discussion

In $\text{RE} = \text{La-Gd}$, RE_2O_3 or Pr_6O_{11} and CuO were mixed under the RE/Cu atomic ratio of 2. The mixture was heated for 2 h at various temperatures, as described in the experimental section. Characterization of the product at each temperature by the XRD measurement revealed the formation of RE_2CuO_4 single phase at 800°C or above. As shown in Fig. 1 summarizing the XRD patterns obtained at 800°C, crystal structure of La_2CuO_4 was orthorhombic, and that of other RE_2CuO_4 ($\text{RE} = \text{Pr, Nd, Sm and Gd}$) was tetragonal.

When the heavier rare earth oxide (RE_2O_3 , $\text{RE} = \text{Dy, Ho, Er and Yb}$) or Y_2O_3 were mixed with CuO in the $\text{RE}_2\text{O}_3/\text{CuO}$ or $\text{Y}_2\text{O}_3/\text{CuO}$ formula weight ratio of 1:2, single phase of $\text{RE}_2\text{Cu}_2\text{O}_5$ was formed at 1000°C or above (Fig. 2). From the analysis of the XRD patterns of the products prepared at 1000°C, all of the $\text{RE}_2\text{Cu}_2\text{O}_5$ were found to assume an orthorhombic structure.

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Fig. 1. XRD results of RE_2CuO_4 prepared at 800°C. Fig. 2. XRD results of $\text{RE}_2\text{Cu}_2\text{O}_5$ prepared at 1000°C.

The above results that the products for the lighter and heavier rare earths are RE_2CuO_4 and $\text{RE}_2\text{Cu}_2\text{O}_5$, respectively, are consistent with the report that the pyrolysis of the dinuclear copper(II)–rare earth(III) complexes, $\text{CuRE}(\text{dhbean})(\text{NO}_3)(\text{dmsO})_m(\text{H}_2\text{O})_n$, affords the $(\text{RE}_2\text{CuO}_4 + \text{CuO})$ mixture for RE = La–Gd and the single phase of $\text{RE}_2\text{Cu}_2\text{O}_5$ for RE = Tb–Lu.¹²⁾

Figure 3 shows TG–DTA curves of the (carbon black + the as-purchased CuO powder) mixture, where the amount of carbon black is 5 wt %. The weight was gradually decreased from the

Fig. 3. TG–DTA curves of (carbon black + the as-purchased CuO powder) mixture.

Fig. 4. DSC curves of carbon black, (carbon black + the as-purchased CuO powder) mixture, (carbon black + CuO calcined at 800°C) mixture and (carbon black + CuO calcined at 1000°C) mixture.

room temperature. An abrupt weight loss occurred in the range of 300 to 420°C and the exothermic DTA peak with a maximum at 417°C was observed. The weight loss, ca. 5%, in the plateau above 420°C is due to the combustion of carbon black. **Figure 4** shows DSC curves of carbon black itself, (carbon black + the as-purchased CuO) mixture, (carbon black + CuO calcined at 800°C) mixture and (carbon black + CuO calcined at 1000°C) mixture. The DSC peak temperature corresponding to combustion of the carbon black was evaluated to be 665°C, and drastically decreased to 413°C when the as-purchased CuO powder without thermal-pretreatment was mixed as a catalyst. Such as-purchased CuO is impractical, since the thermal deterioration of its catalytic activity will take place on exposure to the exhaust gases. For the (carbon black + CuO calcined at 800°C) mixture and the (carbon black + CuO calcined at 1000°C) mixture, combustion temperatures were 509 and 532°C, respectively. The higher the calcination temperature

Fig. 5. DSC curves of (carbon black + La_2CuO_4 prepared at 800°C), (carbon black + Pr_2CuO_4 prepared at 800°C) and (carbon black + $\text{Yb}_2\text{Cu}_2\text{O}_5$ prepared at 1000°C) mixtures.

of the CuO is, the lower its oxidation activity toward carbon black becomes. Specific surface areas of CuO powders as purchased, calcined at 800°C and at 1000°C were estimated to be 0.78 , 0.15 and $0.05\text{ m}^2\cdot\text{g}^{-1}$, respectively. These findings are consistent with the report that the surface area is one of the important factors controlling catalytic performance for diesel particulate combustion.⁷⁾

Figure 5 shows three typical DSC curves of the (carbon black + orthorhombic La_2CuO_4 prepared at 800°C) mixture and the (carbon black + tetragonal Pr_2CuO_4 prepared at 800°C) mixture. These two mixtures give the DSC exothermic peak at 465°C , which was 200°C lower than that (665°C) of carbon black itself and also 44°C lower than that (509°C) of the (carbon black + CuO calcined at 800°C) mixture. Plot of the DSC peak temperatures of a series of (carbon black + RE_2CuO_4 prepared at 800°C) mixtures vs. ionic radii of 8-coordinated RE^{3+} ($\text{RE} = \text{La}$, Pr , Nd , Sm and Gd) is shown in Fig. 6. All of the RE_2CuO_4 prepared at 800°C decreased the combustion temperature of carbon black, compared with the CuO calcined at 800°C , consistent with the measurements that the specific surface areas of RE_2CuO_4 prepared at 800°C were $0.71\text{--}0.89\text{ m}^2\cdot\text{g}^{-1}$ which are higher than that ($0.15\text{ m}^2\cdot\text{g}^{-1}$) of CuO calcined at 800°C . The combustion temperature tends to be decreased with increasing the ionic size of RE^{3+} in the RE_2CuO_4 oxide from $\text{RE} = \text{Gd}$ to $\text{RE} = \text{Pr}$.

Typical DSC curve of the (carbon black + $\text{Yb}_2\text{Cu}_2\text{O}_5$ prepared at 1000°C) mixture is also given in Fig. 5. The DSC peak corresponding to the combustion of carbon black in this mixture appeared at 548°C , which is 117°C lower than that (665°C) of carbon black. Figure 6 shows the plot of DSC peak temperatures for the (carbon black + $\text{RE}_2\text{Cu}_2\text{O}_5$ prepared at 1000°C) mixtures against the ionic radii of 8-coordinated RE^{3+} ($\text{RE} = \text{Dy}$, Ho , Er , Yb and Y). As can be seen from this Figure, when the $\text{RE}_2\text{Cu}_2\text{O}_5$ oxides were adopted, opposite results from the RE_2CuO_4 prepared at 800°C were obtained as follows: DSC peak temperatures ($548\text{--}558^\circ\text{C}$) of the (carbon black + $\text{RE}_2\text{Cu}_2\text{O}_5$ prepared

Fig. 6. The dependence of DSC exothermic peak temperatures for (carbon black + RE_2CuO_4 prepared at 800°C) mixture ($\text{RE} = \text{La}$, Pr , Nd , Sm and Gd) and (carbon black + $\text{RE}_2\text{Cu}_2\text{O}_5$ prepared at 1000°C) mixture ($\text{RE} = \text{Dy}$, Ho , Er , Yb and Y) on ionic radii of the 8-coordinated RE^{3+} .

at 1000°C) mixtures were higher than that (532°C) of the (carbon black + CuO calcined at 1000°C) mixture, and showed a tendency to be increased with increasing the ionic size of RE^{3+} , though the difference of DSC peak temperatures was only 10°C from the minimal 548°C for $\text{RE} = \text{Yb}$ to the maximal 558°C for $\text{RE} = \text{Dy}$.

As shown in Figs. 4 and 5, shape of the DSC curve and half width of the DSC peak differ, depending on the kind of catalyst mixed with carbon black. Such difference may be caused by the structural change of catalysts which affects the evolution temperature and amount of active oxygen from each catalyst. Further researches including the mechanisms of oxidation activity for carbon black are in progress for the low temperature combustion of soot.

4. Conclusion

Mixed metal oxides, RE_2CuO_4 ($\text{RE} = \text{La}$, Pr , Nd , Sm , Gd) and $\text{RE}_2\text{Cu}_2\text{O}_5$ ($\text{RE} = \text{Dy}$, Ho , Er , Yb , Y), were prepared, and their oxidation activity for carbon black was examined by using the differential scanning calorimeter (DSC).

- (1) In $\text{RE} = \text{La}\text{--}\text{Gd}$ series, RE_2CuO_4 single phase was obtained above the calcination temperature of 800°C , when RE_2O_3 or Pr_6O_{11} and CuO were mixed under the RE/Cu atomic ratio of 2. The crystal structure of La_2CuO_4 was orthorhombic and that of the other RE_2CuO_4 ($\text{RE} = \text{Pr}\text{--}\text{Gd}$) was tetragonal. For the $\text{RE} = \text{Dy}\text{--}\text{Yb}$ series, $\text{RE}_2\text{Cu}_2\text{O}_5$ single phase was obtained by calcining above 1000°C and their crystal structure was orthorhombic.
- (2) The DSC peak temperature corresponding to combustion of the carbon black was decreased to 413°C by mixing the as-purchased CuO powder, whereas carbon black itself was oxidized at 665°C . However, the as-purchased CuO powder is impractical, because of its thermal deterioration in the catalytic activity on exposure to the exhaust gases. When the carbon black was mixed with

the CuO powder calcined at 800 and 1000°C, combustion occurred at 509 and 532°C, respectively.

- (3) When carbon black was mixed with RE_2CuO_4 (RE = La, Pr, Nd, Sm, Gd) prepared at 800°C, combustion temperature of the carbon black was 509°C for RE = Gd which was similar to that for the (carbon black + CuO calcined at 800°C) mixture. From 509°C, combustion temperature was almost linearly decreased to 465°C for RE = Pr and La with increasing the ionic radius of RE^{3+} .
- (4) When carbon black was mixed with $\text{RE}_2\text{Cu}_2\text{O}_5$ (RE = Dy, Ho, Er, Yb, Y) prepared at 1000°C, opposite results were obtained. Combustion temperature (548–558°C) of the (carbon black + $\text{RE}_2\text{Cu}_2\text{O}_5$ prepared at 1000°C) mixtures were higher than that (532°C) of the (carbon black + CuO calcined at 1000°C) mixture, and showed a tendency to be increased with increasing the ionic size of RE^{3+} , though the difference of DSC peak temperatures was only 10°C from the minimal 548°C for RE = Yb to the maximal 558°C for RE = Dy.
- (5) In the present RE–Cu–O mixed oxides, the combustion temperature was decreased to 465°C for La_2CuO_4 and Pr_2CuO_4 which showed the highest carbon oxidation activity.

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