

Freeze-Drying of Copper-Oxide-Based Porous Bulk Catalysts for Diesel Soot Combustion

Toshiyuki Yokota, Masafumi Sakota, Yoshihiro Matsuda,
Tetsuo Katsuyama and Yasuyuki Takahata

Department of Chemistry and Chemical Engineering,
Faculty of Engineering, Yamagata University

(平成16年10月4日受理)

Abstract

Porous copper oxide particles were prepared by freeze-drying to serve as bulk catalysts for diesel soot combustion. Frozen particles of aqueous copper sulfate solution mixed with other metal sulfate solutions were dried in a vacuum chamber, and the dried particles were calcined into metal oxide particles. The open porosity induced by sublimation of ice crystals in the freeze-dried particles was retained during calcination and subsequent sintering. These porous particles were directly utilized as bulk catalyst packed in a diesel soot trap. TG-DTA thermal analysis was employed to evaluate the catalyst activity in oxidation of diesel soot. In order to achieve intimate contact between catalyst and soot, the oxide particles were impregnated with metal chlorides, which are expected to form liquid phase during soot combustion. Among the prepared catalysts, CuO/Cu₂O with KCl/LiCl exhibited noticeable activity and durability, exhibiting an ignition temperature of 300°C in soot combustion.

1. Introduction

Emissions of nitrogen oxides and particulate soot from diesel engines present a severe environmental problem. Soot emission can be reduced by placing a trap and/or an oxidation catalyst within the exhaust stream. The combination of trap and oxidation catalyst appears to be the most plausible after treatment technique for eliminating soot particles.

A variety of materials have been tested as soot oxidation catalysts. Single metal oxides, selected mixtures thereof, and double oxides such as perovskite-type and spinel-type oxides have shown soot oxidation activity^{1, 2, 3, 4}. Copper oxide is one of the active catalysts for diesel soot combustion. Some mixtures of copper and other

metal oxides have been also tested^{5, 6, 7, 8}.

The intensity of contact between soot and catalyst has been said to be one of the major parameters controlling the activity of soot combustion catalyst. Neft *et al.*⁹ studied the effect of two types of contact: tight contact, where catalyst and soot were milled in a mortar, and loose contact, where catalyst and soot were loosely mixed with a spatula, on the combustion temperatures for various metal oxide catalysts. They also reported that under practical conditions poor contact was achieved between soot and catalyst, resembling the loose contact mentioned above.

In this study, porous bulk catalysts based on copper oxide were processed by freeze-drying^{10, 11}, and their application to diesel

soot combustion was examined. The TG-DTA technique was adopted to estimate ignition temperature, which was employed as an index for evaluating the activity of the catalysts^{6,7)}. The catalyst was impregnated with metal chlorides that are converted into a eutectic mixture. The eutectic mixture formed a liquid phase that promoted intimate contact between soot and catalyst. Catalyst activity was assessed by comparing activation energy measured by Ozawa's method^{3, 8, 12)}, and catalyst stability was evaluated by repeated soot combustion tests¹³⁾.

2. Experimental

An aqueous copper sulfate solution ($1.5\text{mol}/\text{dm}^3$) was prepared as starting feed material for freeze-dry processing. Other aqueous sulfate solutions ($2\text{mol}/\text{dm}^3$) of NiSO_4 , CoSO_4 , VOSO_4 , and $\text{Ce}(\text{SO}_4)_2$ were arranged and mixed with the copper solution (Metal/Cu mole ratio = 1:1) to obtain copper oxide-based mixtures. Drops of the starting feed aqueous solution were frozen in a liquid nitrogen bath, and the frozen particles were transferred into a vacuum chamber for drying. The chamber temperature was regulated so as to allow sublimation of the ice crystals. Upon sublimation, the ice crystals left behind open pores of the micron order. The dried particles were calcined and sintered in a muffle oven. Heating conditions for calcination were determined for each sulfate to decompose into the oxide. The fired oxide particles measured roughly 1~2mm in diameter and had a porosity of about 0.7. The particles structures were observed by scanning electron microscopy (SEM), and their compositions were determined by X-ray diffraction (XRD).

The freeze-dried porous metal oxide particles were impregnated with a mixed solution of metal chlorides. The chlorides were expected to function as a co-catalyst that promotes catalytic activity and, furthermore, encourages intimate contact between soot and catalyst by forming a liquid phase

in a soot combustion process. A mixed aqueous solution of KCl and LiCl was used for the impregnation. Afterwards, drying treatment was carried out at 120°C for 2 hours. The composition of the mixed solution was arranged to form a eutectic mixture with a mole ratio of $\text{KCl}/\text{LiCl}=0.41/0.59$ ¹⁴⁾. The chlorides mixture shows a eutectic temperature of 355°C , despite KCl having a melting point of 771°C and LiCl having a melting point of 610°C . The quantity of impregnated chlorides was adjusted to 10 wt%.

Activity of the prepared catalysts was assessed by TG-DTA. The porous particles were ground in a mortar and mixed with diesel soot or amorphous carbon powder (catalyst/soot or catalyst/carbon mass ratio = 1:0.2). The soot was collected from a motor vehicle equipped with a diesel engine, and commercially available carbon powder (Cica-Reagent, extra pure grade) was used as model soot. These mixed samples were utilized for the tight-contact experiments. The loose-contact samples were prepared by mixing the ground oxide powder with soot or carbon powders by means of a spatula. These samples were subjected to TG-DTA for the assessment of combustion temperature. The samples were heated at $10^\circ\text{C}/\text{min}$, up to the temperature of complete soot or carbon combustion. The activation energy of the soot combustion was measured by Ozawa's method^{3,8,12)} using TG data obtained at various heating rates within the range of $10 - 40^\circ\text{C}/\text{min}$. The stability of the catalyst was confirmed by repeated combustion tests. The catalyst used for a TG-DTA experiment was removed and mixed again with carbon powder, and the mixture was again subjected to TG-DTA. This series of combustion cycles was repeated for a total of ten rounds.

3. Results and discussion

First, the combustion properties of diesel soot were examined by DTA. The results are shown in Figure 1. Three exothermic peaks, attributed to

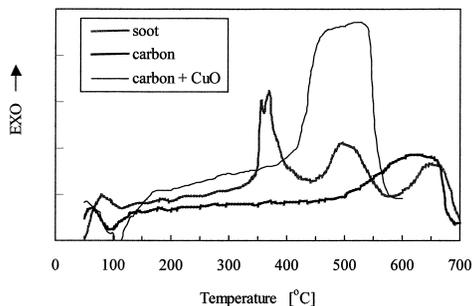


Figure 1. DTA curves for combustion of soot, carbon, and carbon with CuO.

SOF (soluble organic fraction) sulfates, and particulate carbon, are observed. The last peak, at 650°C, is due to the carbon particles, which act as a flame retardant material in the diesel soot. Therefore, in the subsequent catalyst tests we adopted amorphous carbon powders instead of diesel soot as the model material. The DTA curve in the carbon powder combustion is also shown in Figure 1. The exothermic reaction started at 520°C and ended at 680°C. The exothermic peak is almost identical with the last peak of diesel soot combustion.

Next, the catalytic activity of the copper oxide prepared was examined for carbon combustion. The catalyst mixed with the carbon powders was subjected to TG-DTA; the DTA curve is shown in Figure 1. The exothermic peak appears at a lower temperature than in the case of carbon combustion without the catalyst. The height and broadness of the peak were dependent on the amount of carbon in the sample. From the results, we chose the ignition temperature; i.e., the rising temperature of the exothermic peak for evaluation of catalyst activity.

Subsequently, we assessed catalytic activity of other metal oxides, such as vanadium and cerium oxide, and the mixed and double oxides, such as Cu/Co, Cu/V, Cu/Ce, Cu/Ni, and Co/Ni oxide for amorphous carbon combustion. Table 1 shows the ignition temperatures evaluated by DTA curves. The table also shows the relative compressive strength of each porous particle. The

Table 1. Ignition temperatures of carbon combustion for metal oxide catalysts and relative compressive strength

Chemical formula of catalyst	Ignition temperature [°C]	Relative compressive strength ^{*)}
CuO	420	+
CuO+Co ₃ O ₄	450	++
CuNiO ₂	460	++
CuO+V ₂ O ₅	430	-
CuO+CeO ₂	430	-
V ₂ O ₅	420	-
CeO ₂	510	-
CoNiO ₂	510	++

^{*)} ++, rigid; +, firm; -, fragile, easily broken by picking up with tweezers

particles labeled with (-) were found to be fragile, and unsuitable for fabrication into a DPF trap. In view of these results, we selected Cu/Co and Cu/Ni oxide as candidates for further examination.

Crystal composition of the catalyst given in Table 1 was determined by X-ray diffraction (XRD) analysis. Figure 2 shows the XRD pattern of Cu/Co oxide. The results show that the sample is a mixture of single-copper oxide CuO and cobalt oxide Co₃O₄. The Cu/Ni catalyst constituted a double oxide, CuNiO₂. CuO/Co₃O₄ and CuNiO₂ catalysts exhibit almost the same activity and similar levels of compressive strength; however, sintering temperature to obtain durable strength was more than 1000°C for CuNiO₂ and below 900°C for CuO/Co₃O₄. Thus, we selected CuO/Co₃O₄ as the most desirable catalyst among those prepared in this study.

Figure 3 shows the SEM micrographs of

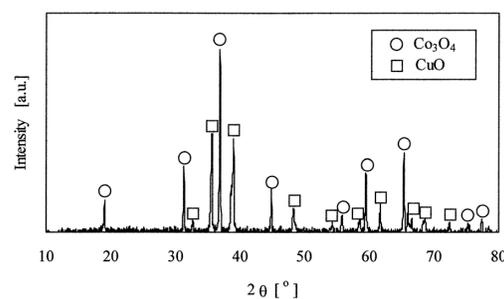


Figure 2. X-ray diffraction pattern of CuO/Co₃O₄ catalyst.

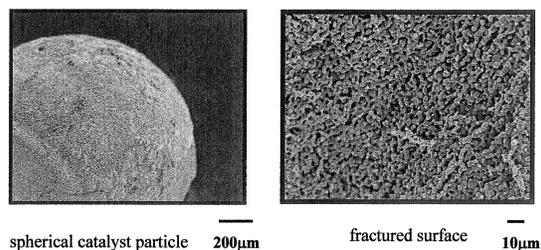


Figure 3. SEM micrographs of $\text{CuO}/\text{Co}_3\text{O}_4$ catalyst.

$\text{CuO}/\text{Co}_3\text{O}_4$ catalyst. Macro open pores of micron order were observed. This open porosity would be convenient for promoting contact between particulate materials in the diesel exhaust gas and the catalyst.

Metal chlorides have often been used as additives or co-catalysts for a soot combustion catalyst, in order to promote catalyst activity. The $\text{CuO}/\text{Co}_3\text{O}_4$ catalyst was impregnated with a KCl/LiCl mixture. The molar ratio of KCl/LiCl was chosen so as to create a eutectic mixture that would form a liquid phase in the temperature range of diesel engine exhaust. Thus, it was expected to achieve intimate contact between particulate materials and catalyst. Figure 4 shows the DTA results for carbon combustion by the $\text{CuO}/\text{Co}_3\text{O}_4$ catalysts with and without the metal chloride additive. The additive was observed to exert magnificent activity promotion. Ignition temperature changed from 450°C to 280°C , which is within the range of the exhaust stream temperature. The amount of the chlorides additive in the catalyst was varied from 10 wt% to 2 wt%, but no significant change in ignition temperature was

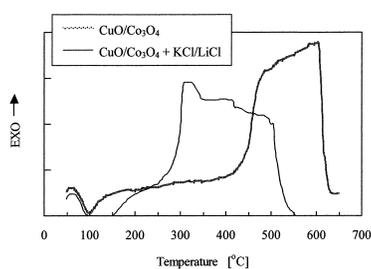


Figure 4. DTA curves of carbon combustion by $\text{CuO}/\text{Co}_3\text{O}_4$ catalysts with and without KCl/LiCl .

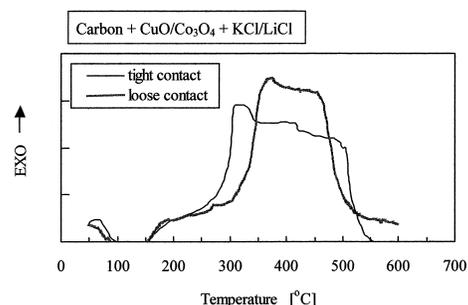


Figure 5. Effect of tight and loose contact on carbon combustion by $\text{CuO}/\text{Co}_3\text{O}_4$ with KCl/LiCl catalyst.

observed.

In the screening of candidate soot oxidation catalysts, intensity of contact between soot and catalyst is one of the important parameters that determine the soot oxidation rate. Two types of contact, intimate (tight) and poor (loose) contact, were studied. Figure 5 shows the results of DTA for tight and loose contact in carbon powder combustion by the $\text{CuO}/\text{Co}_3\text{O}_4$ catalyst with KCl/LiCl . The results show that ignition temperature is slightly lower in tight contact than in loose contact. The diesel soot combustion was effected in the two types of contact, and the results are shown in Figure 6. In this case, the ignition temperatures under the two conditions are almost the same. The KCl/LiCl additive forming a liquid phase could work effectively on soot combustion even in loose contact. This would be very beneficial in practical use of a soot combustion device installed in a diesel vehicle.

For the quantitative evaluation of catalyst

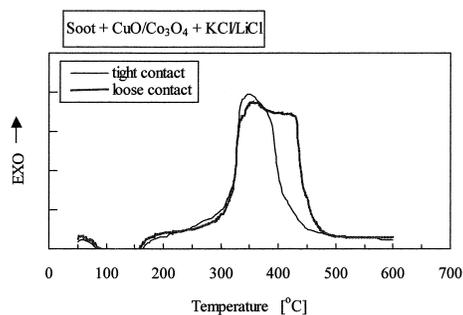


Figure 6. Effect of tight and loose contact on soot combustion by $\text{CuO}/\text{Co}_3\text{O}_4$ with KCl/LiCl catalyst.

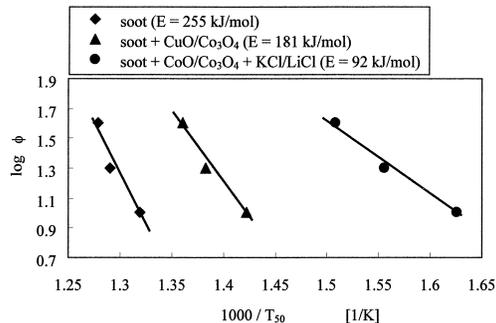


Figure 7. Ozawa plots of soot combustion by the CuO/Co₃O₄ catalysts.

activity, we measured the apparent activation energy for uncatalyzed and catalyzed soot combustion, by Ozawa's method¹²⁾. The TG-DTA data were gathered by changing the heating rate ϕ from 10 to 40K/min. Temperature T_{50} , defined as the temperature at which 50 wt% of soot was burned, was measured from the TG data. Figure 7 shows an Ozawa plot, $\log \phi$ versus $1/T_{50}$. Linear dependence was obtained; apparent activation energy E was calculated from the slope of the straight line, from the following equation³⁾.

$$\log \phi = B - 0.4567(E/RT_{50})$$

The obtained values of activation energy are shown in the figure. These values coincide with those obtained by other researchers^{3, 8)}. The activation energy of the best-catalyzed reaction was 36.1% that of uncatalyzed soot combustion.

The stability of the CuO/Co₃O₄ with KCl/LiCl catalyst was confirmed by ten repetitions of carbon combustion. Ignition temperatures

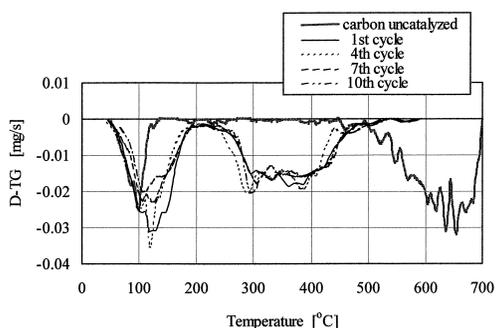


Figure 8. D-TG curves of repeated combustion tests by CuO/Co₃O₄ with KCl/LiCl catalyst.

in the tests remained within 275–285°C. TG data differentiated by time, D-TG, represented a combustion rate. Figure 8 shows D-TG versus temperature curves for the cyclic test, along with the curve of carbon combustion with no catalyst. The peaks around 120°C were due to water evaporation. The combustion with no catalyst started at 510°C and exhibited its highest rate at around 650°C. In contrast, the combustion with catalyst exhibited peaks within the temperature range of 270°C to 410°C. The combustion peak for each cyclic test fell within the same temperature range, indicating that the catalyst maintained its stability during the tests.

4. Conclusions

The performance of copper-oxide-based porous bulk catalysts prepared by freeze-drying was assessed for catalytic combustion of diesel soot. CuO/Co₃O₄ impregnated with a KCl/LiCl eutectic mixture emerged as a promising candidate for diesel soot combustion. Ignition temperature was about 300°C, even when the contact between soot and catalyst was loose. Activation energy assessed by Ozawa's method was found to be 92kJ/mol for soot combustion with the catalyst. This value is only 36% that for uncatalyzed soot combustion. Repeated combustion tests confirmed the stability of the catalyst, indicating that a soot trap packed with this catalyst is capable of burning out the soot in diesel engine exhaust.

Nomenclature

- B = constant
- E = apparent activation energy [kJ/mol]
- R = gas constant [kJ/(Kmol)]
- T_{50} = temperature at 50% conversion of soot combustion [K]
- ϕ = heating rate in TG-DTA [K/min]

References

- 1) J. Neeft, M. Makkee and J. Moulijn: Catalysts for the oxidation of soot from diesel exhaust

- gases. I. An exploratory study, *Applied Catalysis B: Environmental*, 8, pp.57-78 (1996)
- 2) G. Saracco, C. Badini, N. Russo and V. Specchia: Development of catalysts based on pyrovanadates for diesel soot combustion, *Applied Catalysis B: Environmental*, 21, pp.233-242 (1999)
- 3) C. Badini, G. Saracco, N. Russo and V. Specchia: A screening study on the activation energy of vanadate-based catalysts for diesel soot combustion, *Catalysis Letters*, 69, pp.207-215 (2000)
- 4) G. Neri, G. Rizzo, S. Galvagno, M. G. Musolino, A. Donato and R. Pietropaolo: Thermal analysis characterization of promoted vanadium oxide-based catalysts, *Thermochimica Acta*, 381 pp.165-172 (2002)
- 5) F. Ahlstrom and I. Odenbrand: Combustion of Soot Deposits from Diesel Engines on Mixed Oxides of Vanadium Pentoxide and Cupric Oxide, *Applied Catalysis*, 60, pp.157-172 (1990)
- 6) P. Ciambelli, P. Corbo, P. Parrella, M. Scialo and S. Vaccaro: Catalytic oxidation of soot from diesel exhaust gases. I. Screening of metal oxide catalysts by TG-DTG-DTA analysis, *Thermochimica Acta*, 162, pp.83-89 (1990)
- 7) P. Ciambelli, V. Palma and S. Vaccaro: Low temperature carbon particulate oxidation on a supported Cu/V/K catalyst, *Catalysis Today*, 17, pp.71-78 (1993)
- 8) C. Badini, V. Serra, G. Saracco and M. Montorsi: Thermal stability of Cu-K-V catalyst for diesel soot combustion, *Catalysis Letters*, 37, pp.247-254 (1996)
- 9) J. Neeft, O. van Pruissen, M. Makkee and J. Moulijn: Catalysts for the oxidation of soot from diesel exhaust gases. II. Contact between soot and catalyst under practical conditions, *Applied Catalysis B: Environmental*, 12, pp.21-31 (1997)
- 10) T. Yokota, Y. Takahata, T. Katsuyama and Y. Matsuda: A new technique for preparing ceramics for catalyst support exhibiting high porosity and high heat resistance, *Catalysis Today*, 69, pp.11-15 (2001)
- 11) T. Yokota, Y. Kubota, Y. Takahata, T. Katsuyama and Y. Matsuda: Processing of porous metal oxide particles for combustion catalysis by freeze-drying, *J. Chem. Eng. Japan*, 37, pp.238-242 (2004)
- 12) T. Ozawa: Kinetic analysis of derivative curves in thermal analysis, *J. Therm. Anal.*, 2, pp.301-324 (1970)
- 13) C. Badini, G. Saracco, V. Serra and V. Specchia: Suitability of some promising soot combustion catalysts for application in diesel exhaust treatment, *Applied Catalysis B: Environmental*, 18, pp.137-150 (1998)
- 14) L. Cook and H. McMurdie ed.: *Phase Equilibria Diagrams*, The American Ceramic Society, Vol. VII, p.204, USA (1989)