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Research Article

Analyzing Loose Contact Oxidation of Diesel Engine Soot and Ag/CeO$_2$ Catalyst Using Nonlinear Regression Analysis

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Abstract

Loose contact (LC) oxidation kinetics of carbon black (CB) model soot and Ag/CeO$_2$ catalyst was deduced from thermogravimetric analysis (TG) experiments. In the LC mode at ≧750 K, CB particles were likely to be combusted also by non-catalyzed oxidation, especially those particles located far from the catalyst surface, as well as Ag/CeO$_2$-catalyed oxidation. Since the non-catalyzed oxidation is not due to catalytic activity, in order to deduce the catalytic activity from TG data, a nonlinear regression analysis method was proposed in this study to extract only the catalyzed oxidation part of the TG data. It was verified that this was successfully done with the equations used by the very good curve fits to the experimental TG data, and the catalytic activity was correctly obtained from LC samples with various degrees of physical contact between the CB and catalyst.

Keywords: soot oxidation; Ag/CeO$_2$; loose contact; nonlinear regression analysis; curve fitting

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1. Introduction

Air pollution caused by soot emitted from diesel engines is a serious environmental problem. In order to prevent the soot from getting into the atmosphere, the catalyzed combustion of the soot trapped in diesel particle filters (DPF) is performed, normally at high temperature [1]. Since a too-high temperature burn off damages the filters, a highly active catalyst is needed to reduce the combustion temperature. Many catalysts claimed as excellent have been reported, but it is not easy to judge the relative catalytic activities from the reported papers. One indication that can be used to evaluate a catalyst is its activation energy (E_a) for the catalyzed oxidation of model soot. A common technique for the calculation of E_a is the Ozawa method [2]. In this method, E_a is extracted from several thermogravimetric analysis (TG) experiments carried out at different heating rates, such as 10-50 °C/min [3-7]. As for soot oxidation reaction, however, insufficient heat transfer and oxygen diffusion into porous medium can be sometimes a serious problem in acquiring correct TG data [8,9]. Therefore, some TG data, especially taken at fast heating rates,

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could lead to the wrong calculation of E_a by the Ozawa method because the limitations are more significant in such an experimental condition.

Soot accumulated on the surface of DPF is finally combusted on the loaded catalyst at high temperature, and the combustion behaviour is highly affected by the contact condition between soot and catalyst. In laboratory studies, the catalytic activity of model soot oxidation has been evaluated using two different contact modes between the catalyst and model soot: tight contact (TC) and loose contact (LC). As a rough definition, TC is intimate contact whereas LC is poor contact between the catalyst powder and model soot. Experiments by Makkee and Moulijn [10-15] have shown that the degree of physical contact significantly affects the soot combustion temperature in laboratory temperature programmed oxidation (TPO) and thermogravimetric analysis (TG) experiments, and that this leads to difficulty in comparing reported catalytic activities. Van Setten *et al.* [15] suggested that the catalytic activity should be evaluated using a realistic contact of catalyst with the model soot, and it was finally decided that this should be the LC mode obtained by shaking in a sample bottle, mixing with a spatula, and dipping in a soot dispersion. As previously reported, LC samples can be prepared by several methods for laboratory studies. Recently, however, another research group revealed that although LC mode is more close to realistic conditions than TC mode, it is still quite far from the contact condition between soot and ceria catalyst on a commercial silicon carbide filter [16]. Therefore, in order to build a bridge between the real contact and laboratory contact, it is urgently important to make a clear definition of LC mode, such as what is LC and how should the LC activity be evaluated?

In this study, we alternatively suggest the use of nonlinear regression analysis, namely, curve fitting in which only one single experimental TG curve is required to estimate the E_a value. A "single curve" method has been previously reported by Slovak [17]. Reaction order, frequency factor and E_a are simultaneously calculated from a single TG curve by using a special computer program for the nonlinear regression calculation. On the other hand, our proposed method has an advantage that it requires only a function of curve fitting that can be performed even with a standard solver tool in MS Excel. Separately calculated E_a values of non-catalyzed and catalyzed oxidations were next used for analyzing soot oxidation behavior in LC mode in order to discuss the correlation between the degree of contact in the LC mode and LC catalytic activity.

2. Materials and Method

2.1. Sample preparation

Samples that use two different contact modes, loose contact (LC) and tight contact (TC), were prepared. The LC samples were prepared by mixing 0.5 g catalyst powder (2 wt% Ag/CeO_2) and 0.05 g carbon black (CB) (Degussa Printex V, 110 m^2/g, 25 nm) in a 50 mL conical tube using a magnetic stirrer operated at 1200 rpm for 10 to 300 minutes (in the data here, the mixing time is given in parenthesis). Both powders were supplied by Japan Reference Catalyst Society for use in the standard diesel engine soot oxidation reaction. The TC samples used the preparation procedure recommended by the society, in which the catalyst powder and CB were mixed with a mass ratio of 1/1 to 100/1 by grinding with a pestle in a mortar for 10 minutes. The repeatability of samples prepared in this study was reasonably good enough to show the reproductive data of TG-DTA.

2.2. Activity test

About 10 mg of the sample was placed on an aluminum container (diameter = 5.2 mm, height = 5 mm, Epolead Service Inc.) for the TG analysis. The container was placed on an arm of a TG-DTA instrument (SII, EXTRA6000). On the other arm, a container with 10 mg α-Al_2O_3 powder was placed for reference. After 110 °C pre-heating for 1 hour, the sample and reference were heated up to 800 °C under 50 cc/min air flow at a heating rate of 5 °C/min. During the heating, the temperature, and the weight loss were both simultaneously recorded at a rate of 1 data point per second.

2.3. Sample characterization

The sample powder was examined by scanning electron microscope (SEM, Quanta 250 SEM, FEI Corporation). The bulk density was estimated by weighing 200 µL samples several times. The samples were obtained by filling a 1000 µL tubing tip marked to the 200 µL line with sample powder.

2.4. Ozawa method

The activation energy of non-catalyzed CB combustion was calculated by the Ozawa method [2]. In this method, the E_a value is estimated from the TG curves measured at different heating rates by using the equation (1).

$$log(r) = B - 0.4567\frac{E_a}{RT_\alpha} \tag{1}$$

where *r* is a constant heating rate, *B* is a constant, *R* is the gas constant, and T_a is the temperature when the CB combustion conversion is *α*. Plotting *log*(*r*) versus $1/T_a$ gives a straight line, and its slope is used to get the activation energy.

2.5. Nonlinear regression analysis method

During the combustion, the weight loss observed in the thermogravimetric experiment is due to CB (C) depletion by the reaction:

$$C + O_2 \rightarrow CO_2 \tag{2}$$

Based on the fundamental principles of reaction kinetics [18], the rate of reaction is given by the following equation with the assumptions that the reaction is first order with respect to C, and the concentration of O_2 does not affect the reaction rate when O_2 is in large excess (pseudo-zero order) when it is being rapidly supplied into the whole C surface during the thermogravimetric experiment:

$$v = -\frac{d[C]}{dt} = k[C]^\alpha[O_2]^\beta \approx ck[C] \tag{3}$$

where *k* is a reaction rate constant, *c* is a constant, and *α* and *β* are reaction orders with respect to C and O_2, respectively. As for *α* value, some research groups have reported it is 0.7 [9] or 0.8 [19] in the soot combustion processes. According to Stanmore *et al.* [1], soot combustion behavior with the order of around 2/3 could be applied to the shrinking core model in which model the rate of combustion is proportional only to the surface of soot spheres due to the diffusion limitation of oxygen into the inside. Actually, insufficient oxygen diffusion into porous model soot is sometimes observable in soot oxidation experiments and causes a wrong TG data acquisition [8,9]. On the other hand, when oxygen molecules fully diffuse into the internal surface to react, the rate of reaction is almost directly proportional to the C concentration, i.e. *α* = 1 [1,20]. Therefore, in order for the approximation in Eq. (3) to be valid, internal diffusion limitation of O_2 in CB particles should be negligible and also their surface should be always saturated by O_2 during the TG experiments. The approximation is reasonably acceptable in the TG experiments operated at slow enough heating rates, such as ≦5 °C/min.

According to the Arrhenius equation [18], *k* has the following form using the frequency factor (*A*) and activation energy (E_a, for catalyzed or non-catalyzed CB oxidation):

$$k = A\exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

Using Equation (4) in Equation (3) and integrating gives:

$$\int_{[C]_0}^{[C]}\frac{1}{[C]}d[C] = -c\int_{t_0}^{t}\left\{A\exp\left(-\frac{E_a}{RT}\right)\right\}dt \tag{5}$$

where $[C]_0$ is the value of the CB concentration in the sample at time = t_0. At a constant heating rate (*r*) expressed as $r = (T-T_0)/t$, the right hand side is the integral which is the second term in Equation 6. By applying the same approximation as used by Ozawa [2], the integral can be approximated as:

$$\int_{[C]_0}^{[C]}\frac{1}{[C]}d[C] = -\frac{cA}{r}\int_{T_0}^{T}\left\{\exp\left(-\frac{E_a}{RT}\right)\right\}dT \\ \approx -\frac{cA}{r}\left\{\frac{E_a}{R}x10^{\left(2.315-0.4567\frac{E_a}{RT}\right)}\right\} \tag{6}$$

After solving and simplifying the equation, a normalized experimental TG curve, *W*(*T*), is obtained as a function of *T* for a constant value of *r*.

$$W(T) = \frac{[C]}{[C]_0} = 10^{\left\{-\frac{cAE_a}{rR}x10^{\left(2.315-0.4567\frac{E_a}{RT}\right)}\right\}} \tag{7}$$

In addition, the normalized rate of weight loss, namely, the derivative thermogravimetric analysis (DTG) data, is obtained by differentiating Equation (7) and using the normalization as follow:

$$DTG(T) = \varepsilon\left|\frac{dW(T)}{dT}\right| \\ = \varepsilon\left|\frac{0.4567cAE_a^2}{rR^2T^2}x10^{\left\{-\frac{cAE_a}{rR}x10^{2.315-0.4567\frac{E_a}{RT}}+2.315-0.4567\frac{E_a}{RT}\right\}}\right| \tag{8}$$

where *ε* is a normalization constant.

For the case in which catalyzed and non-catalyzed CB oxidation occur at the same time during the TG experiments, the TG and DTG curves observed are the sum of the catalyzed and non-catalyzed oxidation curves, with the catalyzed activation energy (E_{a1}) and non-catalyzed activation energy (E_{a2}).

$$
\begin{aligned}
W(T) &= xW_1(T,E_{a1}) + (1-x)W_2(T,E_{a2}) \\
&= x.10^{\left\{-\frac{cA_1E_{a1}}{rR}x10^{\left(2.315-0.4567\frac{E_{a1}}{RT}\right)}\right\}} \\
&\quad + (1-x).10^{\left\{-\frac{cA_2E2}{rR}x10^{\left(2.315-0.4567\frac{E_{a2}}{RT}\right)}\right\}}
\end{aligned}
\tag{9}
$$

$$
\begin{aligned}
DTG(T) &= \varepsilon\left|\frac{dW(T)}{dT}\right| \\
&= \varepsilon\left|-\frac{0.4567c}{rR^2T^2}\left[\begin{array}{l} A_1E_{A1}^2x.10^{\left\{-\frac{cA_1E_{A1}}{rR}x10^{\left(2.315-0.4567\frac{E_{A1}}{RT}\right)}+2.315-0.4567\frac{E_{A1}}{RT}\right\}} \\ +A_2E_{A2}^2x.10^{\left\{-\frac{cA_2E_{A2}}{rR}x10^{\left(2.315-0.4567\frac{E_{A2}}{RT}\right)}+2.315-0.4567\frac{E_{A2}}{RT}\right\}} \end{array}\right]\right|
\end{aligned}
\tag{10}
$$

where x and (1-x) are the ratios of CB weight losses by the catalyzed and non-catalyzed oxidation reaction, respectively.

3. Results and Discussion

3.1. Non-catalyzed CB combustion

The Ozawa method is an excellent way to get an activation energy by using several thermogravimetric curves obtained at different heating rates. Ozawa [2] originally discussed its validity with the examples of the decomposition of calcium oxalate and degradation of nylon 6. It has proved to be a powerful method to get E_a, esp. for the degradation reaction of polymer materials. In this study, we dealt with the oxidation reaction of CB. In this reaction, the reactants were CB and O_2, which is different from the degradation of one single reactant. Therefore, in order to apply the Ozawa method in this reaction system, the experimental TG curves used for the calculation of E_a should be measured under experimental conditions that gives enough oxygen for it to be in excess during the oxidation. We verified that this condition was satisfied by comparing E_a calculated from different experimental data sets. Figure 1 shows the non-catalyzed CB combustion curves of TG and DTG measured at the different heating rates of 2, 5, 10, 20 °C/min.

The Ozawa plot obtained by using all the four curves is shown in Figure 2(a). This showed very good linearity with >0.99 coefficient of regression for all conversions of 20-80%. The calculated E_a values are plotted in Figure 2(b) as a function of conversion, and these showed an increasing trend with conversion increase. However, as a fundamental quantity [18], the activation energy should be constant in the small temperature range used here due to the domination of the exponential term. Therefore, there must be something wrong with the experimental data used for the calculation. We suggest that this was due to the data measured at the faster heating rates, which was caused by the diffusion limitation of oxygen diffusing into the carbon particle resulting from a too-fast combustion reaction. It also probably caused heat transfer limitation due to the large reaction heat emitted during the combustion. The evidence for this was from the comparison of the calculated E_a using only two TG curves of heating rates of 2 and 5 °C/min and 10 and 20 °C/min. As shown in Figure 2(b), the increasing trend of E_a was also observed for the TG curves of 10 °C/min and 20 °C/min. On the other hand, regardless of the

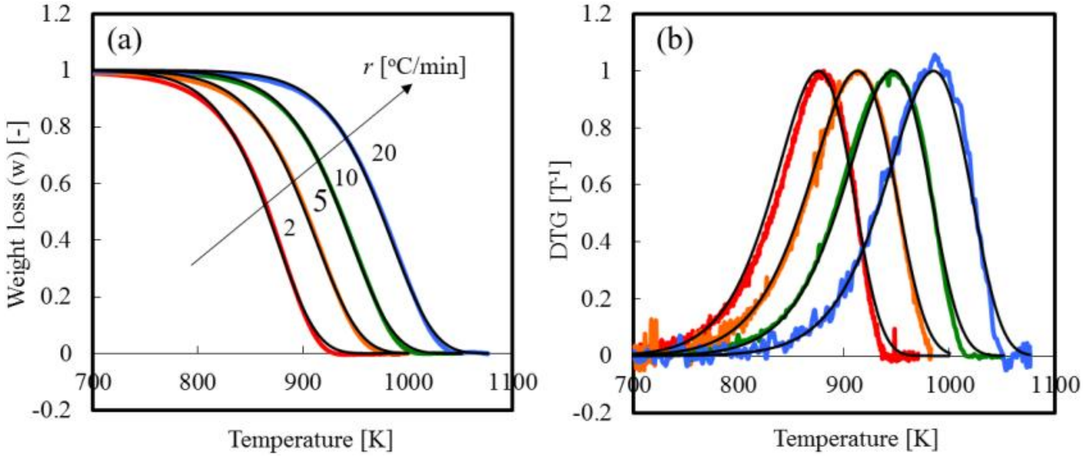

Figure 1. Non-catalyzed CB combustion giving (a) TG and (b) DTG curves measured at the heating rate of 2 (red), 5 (orange), 10 (green), and 20 (blue) °C/min, together with the best fit curves (black lines).

conversion, the calculated E_a values were obtained as an almost constant value of 157 kJ/mol when the TG curves of 2 and 5 °C/min were used. These results showed that inappropriate TG curves were measured when the heating rate was ≧10 °C/min, probably due to the diffusion limitation of oxygen. This result showed that caution is needed even when the Ozawa plot seemed to give good linearity, because the calculated E_a of CB combustion can possibly be wrong. There can be experimental error due to that the TG curves were measured at too fast heating rates, ≧10 °C/min in our case, because the Ozawa method requires the second gaseous reactant to be in large excess.

An improvement can be made by using several TG curves measured at sufficiently slow heating rates, such as ≦5 °C/min, but this is experimentally difficult. Another way that was suggested by Neeft *et al.* [9] is to dilute the sample by inert materials with a high heat capacity and a high thermal conductivity, such as silicon carbide. Their method is highly effective in order to reduce the influence of heat transfer limitation, but at the same time, the dilution causes low resolution in acquired data, especially when a catalyzed E_a value is calculated from TG curves measured with a sample of high Cat/CB ratio. In this study, we alternatively suggest the use of nonlinear regression analysis, namely, curve fitting in which only one single experimental TG curve is required to estimate the E_a value. This method used Equations (7) and (8). In these equations, the normalized TG curve (w) is expressed as a function of temperature, and is obtained at a constant heating rate (r). By using parameter estimation for E_a by fitting by the least squares method to an experimental TG curve measured at a constant heating rate, the E_a value is extracted.

The best fit curves are shown in Figures 1(a) and (b) as black lines, and the corresponding E_a values obtained at each heating rate are summarized in Table 1. As a result, the same E_a values of 174 kJ/mol were separately obtained from the curve fitting used on the experimental data obtained at 2 °C/min and 5 °C/min. This result indicated that the presented method and experimental data were both accurate enough. The E_a values obtained using the data obtained at 10 °C/min and 20

Table 1. Parameters taken for non-catalyzed CB combustion estimated by the method that used Equation (7)

r [°C/min]	E_a [kJ/mol]	cA [-]	R^2
2	175	1.77×10^4	0.9994
5	174	1.28×10^4	0.9994
10	190	8.63×10^4	0.9997
20	205	4.12×10^5	0.9998

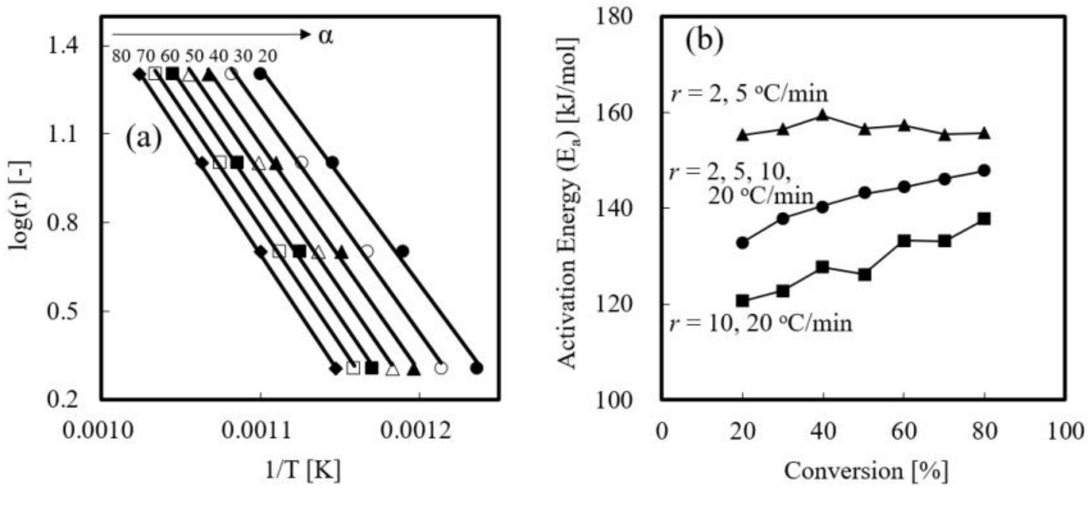

Figure 2. (a) Ozawa plot at the conversion of 20(●), 30(○), 40(▲), 50(△), 60(■), 70(□), and 80 %(◆), and (b) activation energies calculated from the TG curves from 4 heating rates (●), 2 slower heating rates (▲), and 2 faster heating rates (■).

°C/min were quite different from those at 2 °C/min and 5 °C/min, and further showed an increasing trend with heating rate increase, indicating that the combustion reaction proceeded at a faster rate, possibly causing the diffusion limitation of oxygen.

3.2. Catalyzed CB combustion in tight contact mode

In the previous section, CB combustion with no catalyst was discussed to verify the use of a new method that only used one heating rate. Also, it was argued that the experimental condition has to use a heating rate ≦ 5 °C/min in order to get correct E_a values. In this section, we report the determination of the E_a value of a catalyzed reaction proceeding on the surface of a heterogeneous catalyst using the method.

Figure 3 shows the experimental data obtained at 5 °C/min with tight contact samples of Cat/CB = 1/1, 2/1, 10/1, 50/1, and 100/1. With the samples with a higher ratio, CB was burned off at lower temperatures, and the samples of Cat/CB = 50/1 and 100/1 gave the same sharp DTG peaks at 650 °C. This result suggested that over these samples, most CB were combusted by catalysis occurring on the catalyst surface. On the other hand, the samples of Cat/CB = 1/1 and 2/1 showed CB combustion behavior to a higher temperature than the starting temperature of non-catalyzed CB combustion (750 K, denoted by a dotted line in Figure 3(b)), which indicated that for these samples, CB was combusted by the non-catalyzed reaction as well as the catalyzed reaction. Therefore, we should use an experimental TG curve measured with a high ratio Cat/CB sample, Cat/CB = 50/1 in our case, in order to correctly extract the E_a value of the catalyzed reaction by curve fitting. In some samples with Cat/CB ≧ 10/1, a small weight loss was observed up to 510 K and the amount depended on the Cat/CB ratio. This weight loss could result from water loss from the catalyst itself and this loss was intrinsically different from those losses ascribed to CB combustion by catalysis that was observed as an abrupt weight loss in the TG curves or sharp peaks in the DTG curves. Therefore, when the E_a value of the catalyzed reaction was estimated, the TG curve used for the curve fitting did not include the part with the low temperature small weight loss. The best fitted curves using Equations (7) and (8) are shown in Figure 4. As can be seen, Equations (7) and (8) gave very good fits to the experimental data, and the estimated E_a value was 127 kJ/mol.

3.3. Catalyzed CB combustion in loose contact mode

The CB combustion behavior in the LC mode was investigated by TG experiments. The results obtained are shown in Figure 5 for LC samples prepared with a mixing time of 10 to 300 min, together with a TC sample result for reference. As clearly seen in the figure, the weight loss curve corresponding to CB combustion was completed at a lower temperature when the mixing time used was longer, and the temperature converged to the TC result for the LC(300) sample. Since non-catalyzed CB oxidation did not start until the temperature reached 750 K, this suggested that the weight loss observed at ＜750 K corresponded to CB

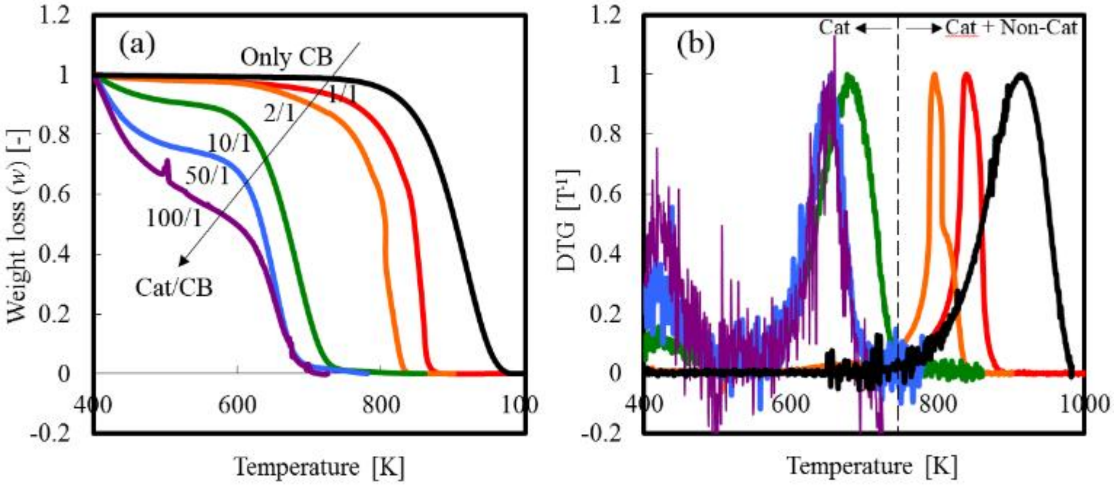

Figure 3. Catalyzed CB combustion giving (a) TG and (b) DTG curves measured at a heating rate of 5 °C /min with TC samples of Cat/CB = 1/1 (red), 2/1 (orange), 10/1 (green), 50/1 (blue), 100/1 (purple) and only CB (black).

combustion by Ag/CeO_2-catalyzed oxidation, while at ≧750 K, CB was combusted by non-catalyzed oxidation as well as catalyzed oxidation. The latter dual oxidation behavior probably occurred in the LC(10), LC(30) and LC(60) samples at ≧750 K.

The different CB combustion behavior observed in the TG experiments of the different LC samples was attributed to the different degree of contact between the catalyst and CB. Figure 6 shows SEM images of the LC(30) and TC samples. In both images, it can only be seen that most of the space in the samples were occupied by catalyst particles, colored in white, and it was difficult to discriminate a difference between the LC and TC samples from the SEM observation. Next, the bulk density was compared for the samples. Figure 7 shows the comparison of 0.1 g volume of sample filled in tubing tips. Table 2 summarizes the sample density measured by the procedure given in the experimental section. Since CB has a smaller density than the catalyst, a mixture of catalyst powder and CB with a mass ratio of 10/1 would give a density midway between these. On visually inspecting the sample volume of LC and TC, a clear difference in the sample density was visible. This is shown in Figures 7(b) and (c). The difference became smaller with a longer mixing time. This result suggested that in the LC samples, more bulky CB particles were attached on the catalyst surface, but by mixing well for a longer time, most of these became smaller crushed particles, and finally the surface was occupied mostly by small particles and approached the same contact condition as the TC mode.

CB combustion by both catalyzed and non-catalyzed oxidations occurs at high temperature, especially for the LC mode samples where the contact is poor between the catalyst and CB and some CB particles are located far away from the catalyst surface and can only undergo non-catalyzed oxidation. In this study, we proposed that in order to correctly evaluate the LC catalytic activity, we need to extract only the part in the TG data that was due to catalyzed oxidation. Since the part due to non-catalyzed oxidation is not due to catalytic activity, it has to be excluded. The remaining part due to catalyzed oxidation can then be used for the correct evaluation of the catalytic activity in the LC mode.

By using the obtained activation energies in the previous sections for the catalyzed and

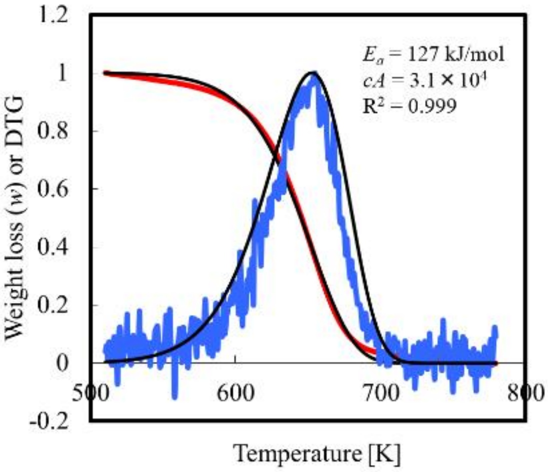

Figure 4. Catalyzed CB combustion TG (red) and DTG (blue) curves measured at a heating rate of 5 °C /min with a TC sample of Cat/CB = 50/1, together with the best fit curves (black lines).

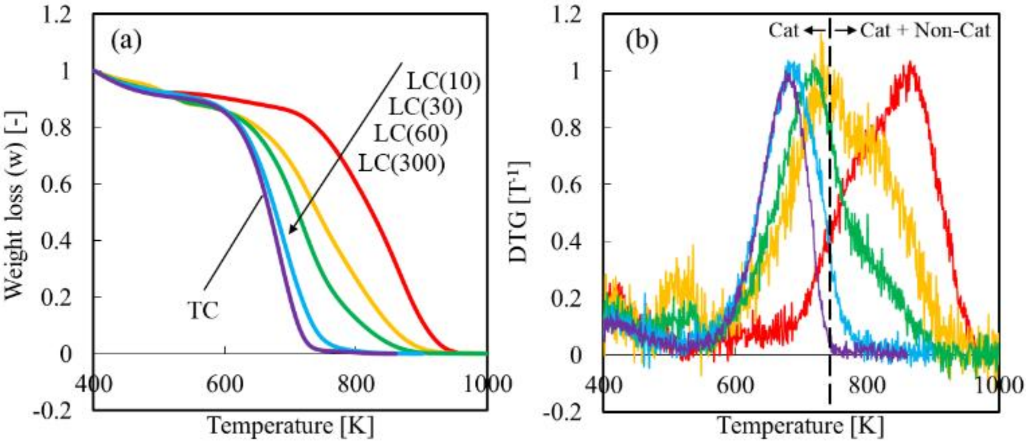

Figure 5. Catalyzed CB combustion giving (a) TG and (b) DTG curves measured at a heating rate of 5 °C /min with LC samples of Cat/CB = 10/1 mixed for 10 (red), 30 (orange), 60 (green) and 300 (blue) min, and a TC sample (purple) reference.

non-catalyzed oxidation as the input parameters, only the catalyzed part were extracted by Equation (9) or (10) from the TG data of LC(10), LC(30) and LC(60). The results are shown in Figure 8. In Table 3, summarized are the parameters taken from the best fitted curves of cA_1, cA_2 and x that is the ratio of the weight loss of CB combusted by catalyzed oxidation. In the curve fitting, the TG and DTG curves did not include the low temperature small weight loss in the same manner as Figure 4. As can be seen, Equation (9) or (10) gave very good fits to the experimental data, and the fitted x value was 0.40, 0.57 and 0.73, respectively, for LC(10), LC(30) and LC(60). In Figure 8(b), the fitted DTG peak seen at the lower temperature corresponded to catalyzed oxidation, while the higher temperature peak was due to non-catalyzed oxidation. The both peaks shifted to a lower temperature with increased mixing time. The peak temperature (T_{max}) change is shown in Figure 9. As the mixing time increased, T_{max} of catalyzed oxidation peaks gradually moved to a lower temperature accompanying the increase in the catalyzed oxidation ratio, and finally approached the T_{max} for the TC sample (where the CB was combusted only by catalyzed oxidation). On the other hand, T_{max} of non-catalyzed CB oxidation peaks approached 750 K that was the starting temperature of non-catalyzed combustion. These trends indicated that the lower LC catalytic activity than the TC activity (= intrinsic catalytic activity) was due to poor contact between the catalyst and CB, and better LC activity was shown by catalysts that can combust more CB due to better contact in the LC mode. In summary, in order to compare the oxidation activity of different catalysts, they need to have same degree of contact between CB and catalyst. Since the degree of contact is easily dependent on the preparation procedure for LC samples, an analytical procedure to use only the catalyzed oxidation part of the TG curve should be followed.

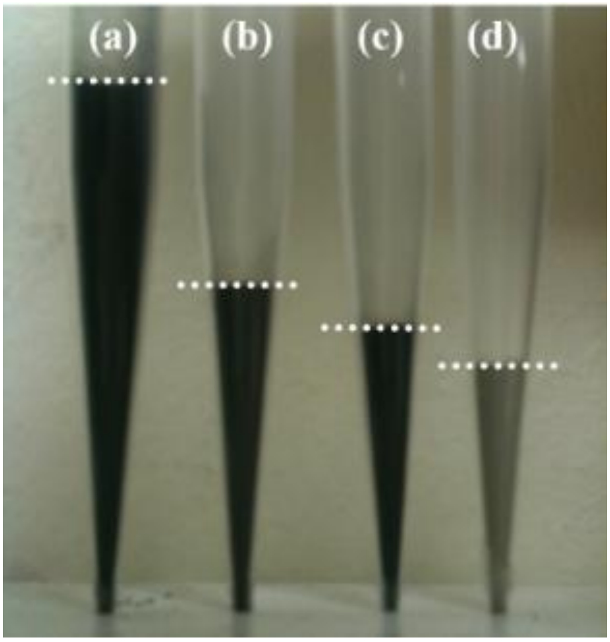

Figure 7. Comparison of 0.1 g volumes of (a) CB, (b) LC(10) sample, (c) TC sample, and (d) catalyst powder.

Table 2. Bulk density of CB and samples of Cat/CB = 10/1

Sample	Bulk density [g/cm^3]
CB	0.20 ± 0.01
TC	0.83 ± 0.03
LC(10)	0.54 ± 0.02
LC(30)	0.56 ± 0.02
LC(60)	0.58 ± 0.02
LC(300)	0.68 ± 0.03

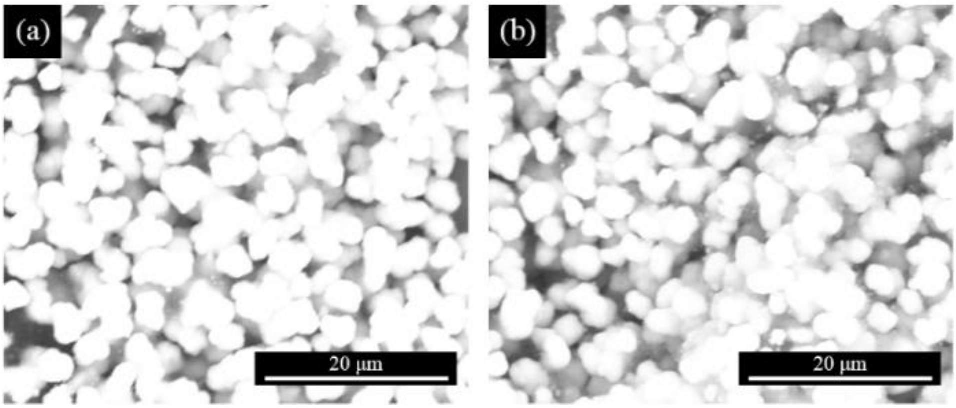

Figure 6. SEM images of (a) LC(30) and (b) TC samples of Cat/CB = 10/1

4. Conclusions

We proposed a nonlinear regression analysis method to use to correctly evaluate the catalytic activity of loose contact (LC) samples of a Ag/CeO_2 catalyst and carbon black (CB). The method is used to extract only the part due to catalyzed oxidation from an experimental TG curve that comprised weight losses due to both catalyzed and non-catalyzed oxidation. This should be done to get the data that represented the “real” CB oxidation by catalysis in the LC mode to give a correct evaluation of catalyst activity. This should be done because the LC activity depended on the condition of the CB particles, such as the bulkiness and physical contact with catalyst, and these can change depending on the mixing time used in the preparation procedure, with a long mixing time giving a result that approached the catalytic activity of the tight contact sample.

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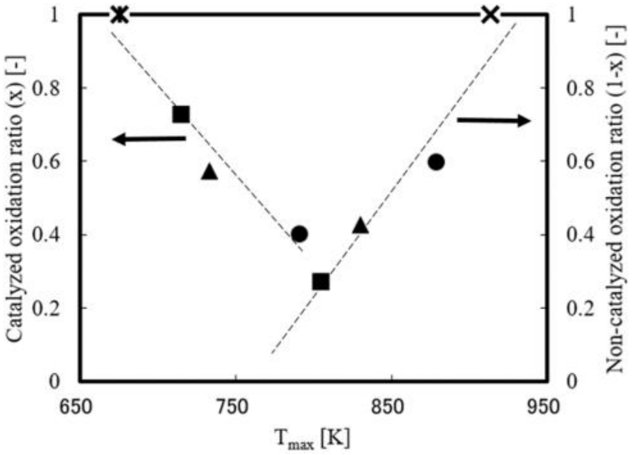

Figure 9. Plots of catalyzed oxidation ratio (x) and non-catalyzed oxidation ratio (1-x) extracted by nonlinear regression analysis versus Tmax. ●: LC(10), ▲: LC(30), ■: LC(60), *: TC, ×: only CB.

Table 3. Parameters used and taken for the catalyzed CB combustion in LC samples estimated by the method that used Equation (9)

Sample	Input parameters		Output parameters			R^2
	E_{a1}	E_{a2}	cA_1	cA_2	x	
LC(10)	127	174	4.0×10^2	3.2×10^4	0.40	0.969
LC(30)	127	174	2.0×10^3	1.4×10^5	0.57	0.854
LC(60)	127	174	3.6×10^3	3.3×10^5	0.73	0.931

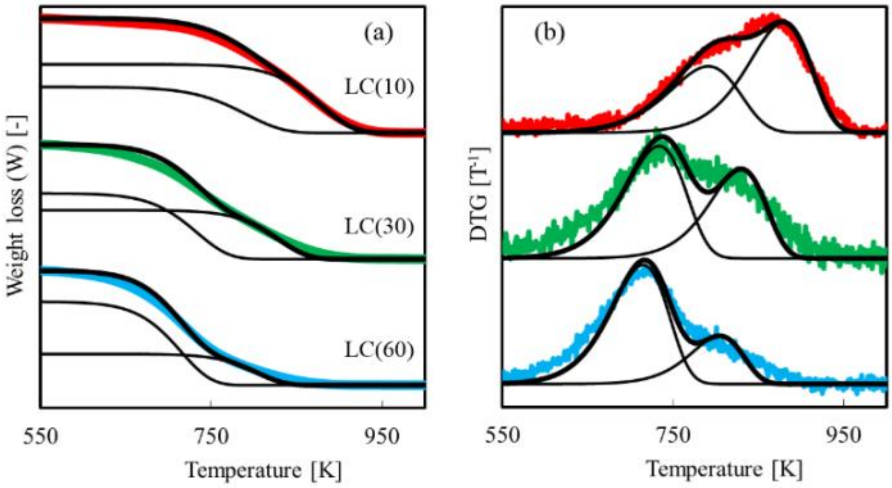

Figure 8. Catalyzed CB combustion (a) TG and (b) DTG curves measured at a heating rate of 5 °C /min with LC samples of Cat/CB = 10/1 mixed for 10 (red), 30 (green) and 60 min (blue), together with the best fit curves (black lines).

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