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Effects of fuel-borne catalysts on kinetics of oxidation of diesel soot generated by pre-mixed pre-vaporized flame

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Abstract. This work reports on the synthesis, characterization and application of organometallic complexes as Fuel Borne Catalysts (FBC). Cerium 2-ethylhexanoate, iron 2-ethylhexanoate and copper 2-ethylhexanoate were used as FBCs. Due to their hydrophobic character, these complexes can be easily solubilized in diesel fuel and converted to metal oxides particles, which efficiently catalyze the oxidation of diesel soot, also known as Particulate Matter (PM). An experimental setup (pre-mixed pre-vaporized flame) was designed and constructed to study the effects of a fuel borne catalyst on the oxidation properties of particulate matter. To better understand the role of metal complexes on soot oxidation, the kinetics of oxidation of metal-containing soot particles was measured. To do this, particulate matter was generated by spraying the catalyst containing the solution and diesel fuel into a mixing chamber. Different concentrations of Fe, Ce and Cu complexes were added to the fuel. The oxidation temperature was reduced by 116°C for the case of 50 ppm Fe, a very important factor in the regeneration of diesel particulate filters. However, an unexpected increase in activation energies was seen. This happens when the process becomes less endergonic with the addition of different sources of FBC. It was also observed that the presence of an iron complex in fuel significantly decreased CO emission during soot oxidation.

1. Introduction

As world demand for energy has increased noticeably in recent years, more effort has been put into finding the most efficient way for energy consumption. In this regard, diesel has gained much attention due to its efficiency compared with other sources [1]. However, because of its particular compression-ignition cycle and its composition, diesel fuel has some problems when used in an engine. Among them, the formation of diesel particulates and their emission into the atmosphere is at the center of much concern and controversy. This is because of their chemistry, which is principally solid particles of carbon and metal compounds with absorbed hydrocarbons, sulfate and aqueous species, and their environmental impact, which makes this issue quite complex.

A Diesel Particulate Filter (DPF) was suggested to eliminate the negative effects of the particulates to some extent [2-6]. But, DPF requires to be periodically regenerated in order to prevent unacceptable back-pressure in the gas exhaust line due to accumulation of particulates in the filter. This regeneration could occur by itself if the operation temperature of the filters were sufficiently high. However, in a typical situation, the exhaust temperature is not constantly

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high enough. Therefore, secondary measures, such as electrically heating to raise the trap temperature or using a catalyst on the wash-coat to reduce the combustion temperature of particulates, have been largely investigated by several researchers. These methods were partially successful, but, some problems, such as catalyst poisoning, were raised in the case of high sulfur content in diesel fuel that led the researchers to use homogeneous catalytic fuel additives in order to generate soot particles that are somehow in contact with metals or metal species. These particulates, which are then trapped in the DPF, are periodically burnt-off. This type of catalyst has been denoted in literature as a Fuel Borne Catalyst (FBC). One of the significant advantages of fuel borne catalysts can be realized in the presence of SO_2, which does not influence the soot oxidation behavior of the catalyst [7].

As the catalytic performance is greatly influenced by the degree of physical contact between the catalyst and PM [8,9], various fuel additives have been considered as a source of fuel borne catalysts. These usually contain active metals (such as Fe, Ce, Cu, Mn, Zn and precious metals [10,11]) as major ingredients, which enhance fuel combustion in the engine cylinder toward complete oxidation, and improve the fuel penalty by decreasing PM emissions. The major obstacle in utilization of these kinds of additives is, however, their solubility and stability in none polar solvents such as diesel. In an attempt to find a suitable catalyst, the use of organometallic complexes has attracted much attention.

An organometallic complex is highly soluble or dispersible in diesel fuel and is synthesized from an organic compound containing at least two functional groups attached to a hydrocarbon linkage. The organometallic complex based on ethylhexanoate is among compounds used for this purpose, as well as for many other applications, such as oxidation, hydrogenation and polymerization and, also, as an adhesion promoter.

In this study, we incorporate different sorts of FBC into the PM network by combusting FBC-blended diesel fuel through a self-constructed experimental set up consisting of a pre-mixed pre-vaporized flame burner. The metal complexes that were employed (Fe, Cu and Ce) are among the most popular in diesel additives, and their concentrations were chosen below environmental restrictions. Direct spraying of diesel fuel blended with a catalyst mixture is considered for simultaneous formation of particulate and metal species, which is more similar to diesel engine conditions than the physical mixing of catalysts and soot used in previous studies. Several sets of experiments have been done to investigate the effects of FBCs on oxidation of particulates from different aspects.

2. Experimental

2.1. Catalyst preparation

Briefly, the catalysts were prepared by the reaction of a mixed solution containing metal nitrates with a solution of NaOH and 2-ethylhexanoic acid, which was stirred for 30 minutes at 80°C. The metal nitrate solution was added drop-wise to the solution of NaOH and 2-ethylhexanoic acid to let the reaction be completed. The precipitate formed was then filtered, washed several times with distilled water and acetone and subsequently dried. The crystals formed as such were recrystallized by solving them in hexane followed by solvent evaporated at 70°C. This way, the following salts were synthesized and used as FBCs; cerium 2-ethylhexanoate, iron 2-ethylhexanoate and copper 2-ethylhexanoate. It should be noted that these salts, within the range of concentrations used in this study, are completely solved in the diesel fuel.

2.2. Synthesis of metal-containing PM

In this study, to investigate the influence of different metals on PM network, a pre-mixed pre-vaporized flame was employed. The physiochemical properties of the diesel fuel used in this study are reported in Table 1.

Figure 1 shows the schematic of the flame burner. The initial concentration of metals in the diesel fuel was adjusted to 0, 20 and 50 ppm. The concentrations were chosen, considering environmental restrictions, and located much lower than previous studies. The diesel fuel stored in the storage column is fed to nozzle 1 by compressor 1. The pressure of compressor 1 was adjusted to 6.9 bar (gauge), which resulted in a flow of 0.5 ml/min through nozzle 1. The line carrying air into the premixing zone is heated with a heater. The flow rate and temperature of air are adjusted to be 10 lit/min and 150°C, respectively, and is mixed with fuel in the premixing zone.

The Air-Fuel Ratio (AFR) should be set to a level which produces both enough particulate and a stable

Table 1. Physiochemical properties of the diesel fuel used in this study.

Density @ 150°C	0.820-0.860 kg/L
Flash point (min)	54°C
Total sulphur (max)	500 ppm
Kinematic viscosity @ 37.8°C	2.0-5.5 mm^2/s
Cloud point (max)	1.5°C
Pour point (max)	-4°C
Carbon residue (max)	0.10 wt%
Ash (max)	0.01 wt%
Water & sediment	0.05 vol%
Cetan index (min)	50

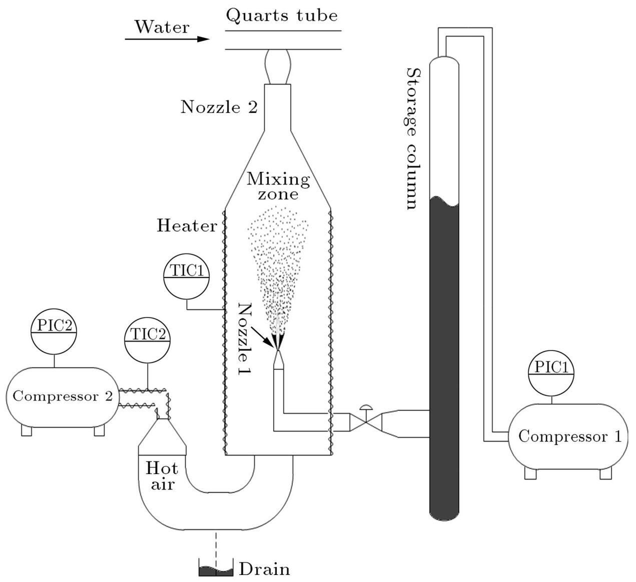


Figure 1. A schematic of pre-mixed pre-vaporized flame that was employed in the present study for synthesizing metal containing PM.

flame. In this case, AFR was 23.8, i.e. above the stoichiometric value (14.6) and similar to the lean burn ratio of diesel engines. To have a stable flame, the temperature of the air/fuel mixture in the premixing zone was kept at 125°C by means of a heater.

The mixing level was mainly influenced by the evaporation degree of the diesel droplets, which, in turn, were affected by the carrier gas (air) temperature (which was set below the boiling point of diesel to guarantee the simultaneous formation of particulates and the metal species within the FBC), as well as the length of the pre-mixing zone. The air/fuel mixture is mainly concentrated around the centerline of the mixing zone; therefore, the amount of mixture in the vicinity of the wall of the premixing zone is almost negligible. This is mostly due to the dispersion and entrainment of the dispersed phase (diesel droplets). However, a drain is used to prevent the accumulation of diesel droplets at the bottom of the mixing zone.

Downstream of the mixing zone, nozzle 2 was used to increase the flow velocity of the mixture and prevent a flash back of flame. The mixture air/fuel is ignited by an electrical spark located above the mixing zone.

As shown in Figure 1 a quartz tube, cooled internally by tap water flow, was placed horizontally above the flame for collecting PM. It moves back and forth for the steady formation of soot on the quarts tube.

2.3. *Characterization and kinetic measurements of metal-catalyzed PM*

Thermogravimetricanalysis (TGA; EXSTAR Model SII-TG/DTA) was used to measure the oxidation temperature, reaction rates and activation energies of the oxidation of PM metal containing particles. PM obtained from diesel without a catalyst was also used as a base for comparison of the catalytic oxidation behavior. The Temperature Programmed Oxidation (TPO) of different samples of soot was obtained in a quartz reactor located in a tubular furnace, equipped with a PID temperature controller. Zero air was used for the oxidation. 5 mg of sample, diluted with 50 mg quartz powder, were used, and the flow of air was adjusted at 100 ml/min. The reactor temperature was raised from room temperature to 800°C by a ramp rate of 10°C/min. The effluent from the reactor was passed through the gas cell of a FTIR (Bruker Vector22 instrument) equipped with KBr windows. The FTIR was used with a resolution of 5 cm^{-1} in the range of 4000-400 cm^{-1}. The calibration of the FTIR gas cell was performed using known concentrations of carbon monoxide and carbon dioxide.

Table 2. ICP results for the synthesized catalysts.

FBCs	**Physical state of the catalyst**	**Metal amount in the catalyst**
$Ce(C_8H_{15}O_2)_3$	Solid	23.43% (weight percent)
$Cu(C_8H_{15}O_2)_2$	Solid	16.86% (weight percent)
$Fe(C_8H_{15}O_2)_3$	Liquid	2012.6 mg/liter

The percentage of metallic elements in the FBCs was obtained by an inductively coupled plasma-optical emission spectrophotometer (ICP-OES vistra-pro). The results are summarized in Table 2.

These analyses were used to prepare a specific concentration of metal in diesel fuel.

Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) was performed with a Hitachi S-4160 microscope in order to study the morphology of the soot.

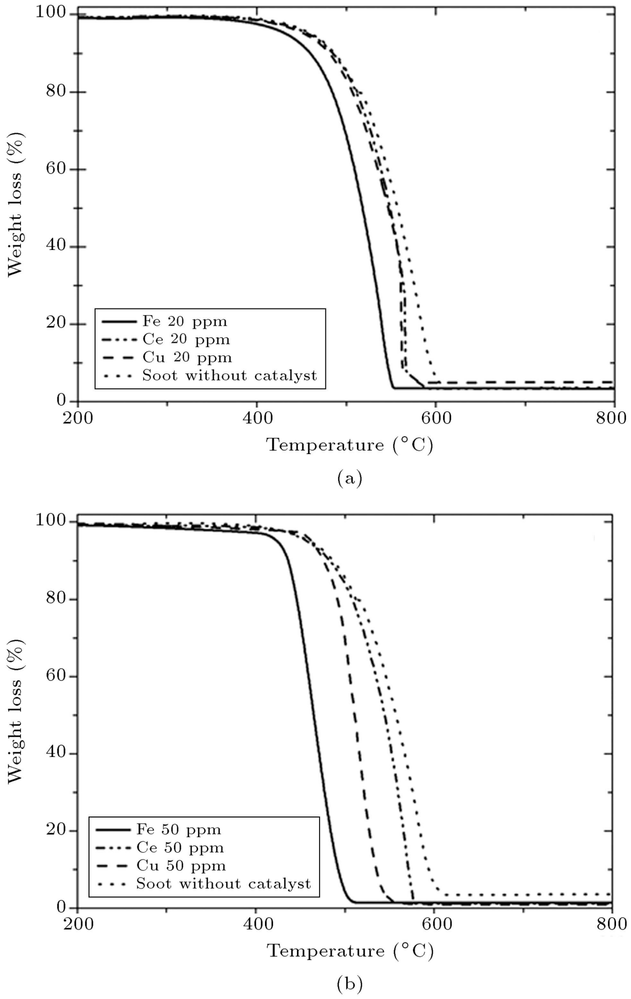
3. Results and discussion

3.1. *Effect of FBCs on soot oxidation*

Thermogravimetric analysis (TGA) is often used as a reliable technique for soot oxidation, since there is a direct relation between weight loss and conversion. For soot oxidation, it is desired to reach the highest conversion level at the lowest possible temperature; this is realized as the most appropriate operating condition for regeneration of DPF. In this study, it was planned to find the temperatures at which the same conversion level is achieved for different FBCs. Also, the temperatures at which the rate of soot combustion was maximum ($T_{\max,\mathrm{DTG}}$) were found from DTG profiles. It should be noted that the activity of a catalyst is inversely proportional to its corresponding $T_{\max,\mathrm{DTG}}$. The results are summarized in Table 3 and the TGA profiles are presented in Figure 2.

Table 3. Temperatures of soot oxidation in presence and absence of catalyst at 5, 50 and 95% weight loss and maximum differential thermogravimetric $T_{\mathrm{DTG,max}}$ (°C).

Concentration (ppm wt)	$T_{5\%}$ **(°C)**	$T_{50\%}$ **(°C)**	$T_{95\%}$ **(°C)**	$T_{DTG,\max}$ **(°C)**
0 ppm	465	557	604	580
Ce 20 ppm	457	554	584	566
Ce 50 ppm	457	544	574	564
Cu 20 ppm	453	546	586	561
Cu 50 ppm	461	515	537	516
Fe 20 ppm	432	518	550	537
Fe 50 ppm	420	461	475	464



(a)

(b)

Figure 2. TGA profiles of (a) soot without catalyst and soot obtained from diesel fuel containing 20 ppm metal, and (b) soot without catalyst and soot obtained from diesel fuel containing 50 ppm metal.

As observed in Figure 2 and Table 3, the temperature for the onset oxidation reaction, i.e. $T_{5\%}$, is considerably lower for soot containing iron. In general, the presence of FBCs has helped various levels of soot oxidation to occur more or less at lower temperatures. The extent of temperature reduction for some cases is about 100°C.

It should be mentioned that the exhaust gas temperature for some heavy diesel engines running under even low load can exceed 400°C [12]. Thus, these results show the possibility of simultaneous regeneration of DPF in the presence of FBCs.

Temperatures for different levels of conversion depend also on the concentration of FBCs. For iron and copper catalysts, increasing concentration improves temperature reduction, whereas this is not the case for the cerium catalyst. However, some explanation is required to better understand the role of these types of catalyst.

3.2. Kinetics of PM oxidation in the presence of FBCs

Regarding the kinetic parameters for the soot oxidation reaction in the presence of each metal catalyst, the following mathematical formulation is presented based on the TGA results presented in Figure 2.

Soot oxidation is a solid state reaction and its kinetics is described by various equations, taking into account the specific features of their mechanisms.

The reaction rate of solid state reactions, i.e. $d\alpha/dt$, are usually expressed in the following form:

$$d\alpha/dt = k(T)f(\alpha), \tag{1}$$

where t is the time, $k(T)$ is the rate constant, T is temperature and α is a dimensionless number defined as $(W_O - W)/(W_O - W_f)$, in which W_O and W_f are the initial and final mass of the soot samples, respectively. $f(\alpha)$ is used to describe the reaction mechanism [13,14].

All TGA analyses were performed at constant heating rate ($\beta = dT/dt$) of 2°C/min. Thus, Eq. (1) may be transformed into Eq. (2):

$$d\alpha/dT = 1/\beta k(T)f(\alpha). \tag{2}$$

$d\alpha/dT$ is obtained from the TGA profiles in Figure 2 by differentiating with respect to T. For evaluating $f(\alpha)$, different solid contact models, presented in Table 4, may be used [15].

$k(T)$ is substituted by the Arrhenius form, i.e., $A\exp(-E_A/RT)$, in Eq. (2), to form Eq. (3), where A is the pre-exponential factor, E_A is the activation energy, and R is the gas constant:

$$(\beta/f(\alpha))(d\alpha/dT) = A\exp(-E_A/RT). \tag{3}$$

Eq. (3) is rearranged into the form of Eq. (4) to obtain E_A:

$$\ln(\beta/f(\alpha))(d\alpha/dT) = \ln(A) + (-E_A/RT). \tag{4}$$

The plot of Eq. (4), based on the contracting sphere model, is shown in Figure 3.

Table 4. Various differential solid contact model functions.

Functions $f(\alpha)$	**Solid state process**
$f_1 = 1/2\alpha^{-1}$	One-dimensional diffusion
$f_2 = 1 - \alpha$	Mampel (first-order)
$f_3 = (1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$	Three-dimensional diffusion
$f_4 = 3(1-\alpha)^{2/3}$	Contracting sphere
$f_5 = (1-\alpha)^2$	Second-order

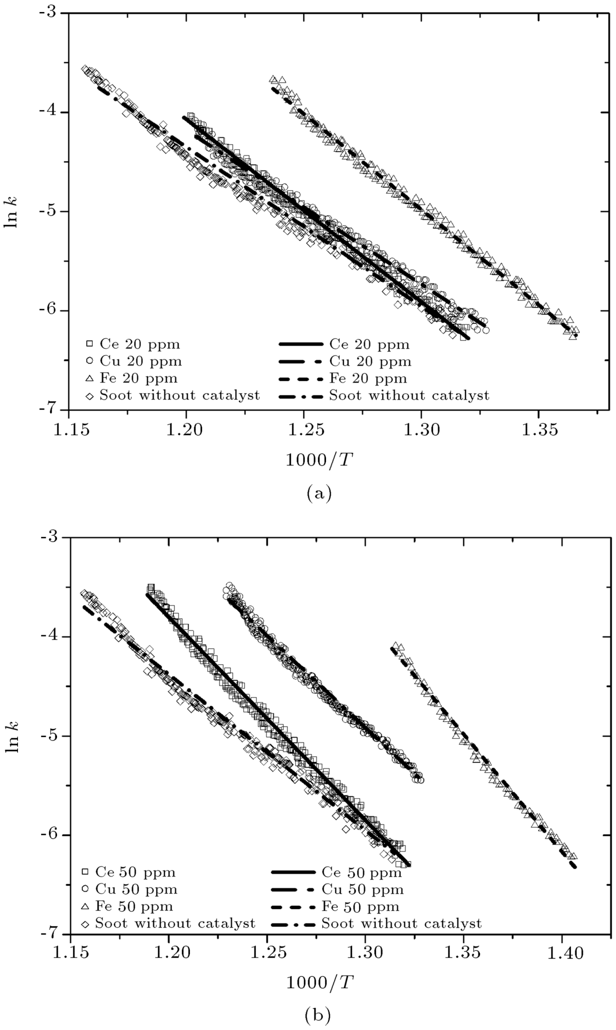


Figure 3. Arrhenius plot for the contracting sphere model: (a) Soot without catalyst and soot obtained from diesel fuel doped with 20 ppm metal; and (b) soot without catalyst and soot obtained from diesel fuel doped with 50 ppm metal.

Thus, the Arrhenius plot shown in Figure 3 can be constructed by plotting the left term in Eq. (4) against the reciprocal temperature ($1/T$); the slope and intercept give $-E_A/R$ and $\ln(A)$, respectively. $d\alpha/dT$ fluctuates considerably at very low-temperatures; hence, the results in Figure 3 are presented only in the range of $0.1 < \alpha < 0.9$, where most of the reactions take place. In the TGA tests, a small ramping rate, i.e. 2°C/min, was selected to generate more data points to choose the proper model. In order to find the most accurate model for this special solid state reaction, linear correlation coefficients (r^2) were calculated and reported in Table 5.

Considering the linear correlation coefficients, it seems that a contracting sphere model would be a proper model for this special solid state reaction. This model was also used by Yong Ho Kim et al. [16] for a similar reaction system. They validated the model by monitoring the morphological changes of the soot particles before and after the partial oxidation reactions. However, some researchers [17] reported that by increasing the concentration of the complex in the fuel, the reaction mechanism would slightly change from one-dimensional diffusion to other possible reaction models. This observation is coherent with the appearance of more than one DTG peak related to the thermal degradation of the prepared soot samples, which was not observed in the present study. Moreover, the SEM micrographs of the soot (Figure 4) reveal that the soot agglomerates containing metal species have similar morphology, i.e. spherical agglomerates with diameters in the range of 5-65 nanometers, which further justifies the use of a contracting sphere model for calculation of kinetic parameters.

The activation entropy change may be calculated according to Eq. (5) [18].

$$\Delta S^{\ddagger} = R\mathrm{Ln}((A.h)/(k_B T_p)), \tag{5}$$

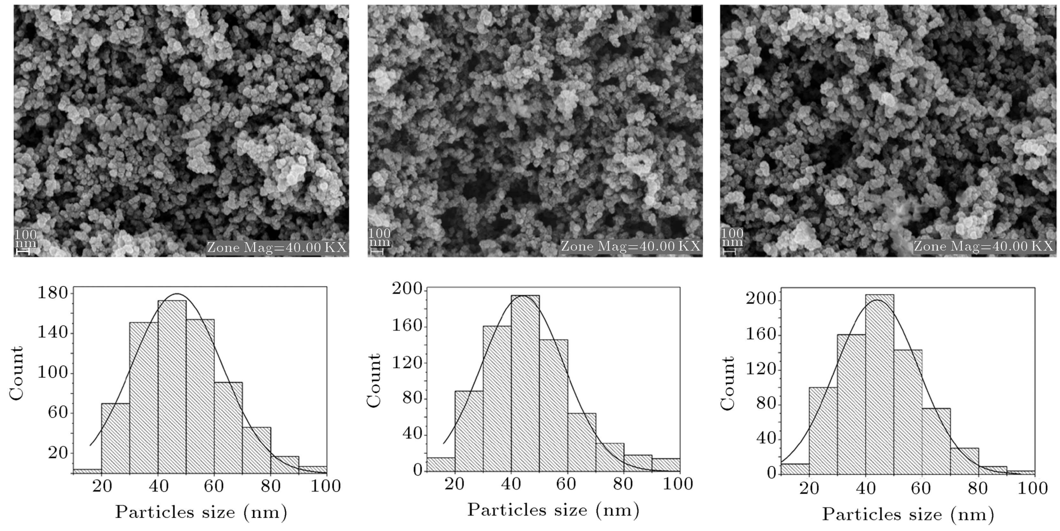
where A is the pre-exponential factor, k_B is the Boltzmann constant ($1.3806 * 10^{-23}$ J K^{-1}), h is the Planck's constant ($6.6260 * 10^{-34}$ J s), and T_p is the average phase transformation temperature peak in the DTG spectra (K). Moreover, the activation enthalpy change ($\Delta H^{\ddagger}$) and activation Gibbs free energy change ($\Delta G^{\ddagger}$), can be calculated from Eqs. (6) and (7):

$$\Delta H^{\ddagger} = E_A - RT_p, \tag{6}$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T_p \Delta S^{\ddagger}. \tag{7}$$

These results are summarized in Table 6.

As seen in Table 6, although a noticeable decrease is observed in the oxidation temperatures, the calculations show an unexpected increase in the activation



(a) (b) (c)

Figure 4. SEM micrographs and size distributions of the soot samples collected after oxidation of the diesel fuel containing metal species: (a) 50 ppm Ce; (b) 50 ppm Cu; and (c) 50 ppm Fe.

Table 5. Linear correlation coefficient for different solid state process.

Solid state process	**0 ppm**	**Ce 20 ppm**	**Ce 50 ppm**	**Cu 20 ppm**	**Cu 50 ppm**	**Fe 20 ppm**	**Fe 50 ppm**
One-dimensional diffusion	0.9792	0.9868	0.9879	0.9859	0.9869	0.9883	0.9917
Mampel (first-order)	0.9498	0.9613	0.9241	0.9761	0.8829	0.9632	0.9665
Three-dimensional diffusion	0.9837	0.9812	0.9753	0.9834	0.9676	0.9905	0.98273
Contracting sphere	0.9897	0.9942	0.9931	0.9899	0.9899	0.9986	0.9969
Second-order	0.9221	0.9441	0.8779	0.9719	0.9217	0.9218	0.9562

Table 6. Kinetic and thermodynamic parameters of the soot samples at different concentration of metal in the diesel fuel derived from contracting sphere model.

Concentration	A (s^{-1})	E_a ($\mathrm{kJ\ mol}^{-1}$)	$\Delta S^{\ddagger}$ ($\mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$)	$\Delta H^{\ddagger}$ ($\mathrm{kJ\ mol}^{-1}$)	$\Delta G^{\ddagger}$ ($\mathrm{kJ\ mol}^{-1}$)
0 ppm	1.36×10^4	129.63	-175.24	122.53	272.03
Ce 20 ppm	6.68×10^5	150.71	-142.41	143.73	263.23
Ce 50 ppm	1.53×10^7	170.32	-115.67	163.35	260.18
Cu 20 ppm	4.37×10^4	133.52	-165.18	126.58	264.36
Cu 50 ppm	6.1×10^6	156.72	-123.22	150.16	247.59
Fe 20 ppm	8.08×10^6	159.81	-121.37	153.07	251.39
Fe 50 ppm	5.3×10^9	194.04	-66.48	187.91	236.97

energies. This happens while the process becomes less endergonic with the addition of different sources of FBCs (which is evidenced by a reduction in the activation Gibbs free energies). So, overall, less energy is required for the soot oxidation in the presence of FBCs, which are considered active compounds for the process. This was also verified before by considerable reduction in the values of $T_{\max,DTG}$. Moreover, the positive values of $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ indicate that the process is endothermic and non-spontaneous.

But it still remains unclear why each metal source has different results in terms of kinetic parameters. In order to find a suitable answer, an EDS test was carried out to analyze the concentration of various metals present in the soot samples collected after oxidation of the diesel containing 50 ppm of metal complexes. The results, summarized in Table 7, show a significant difference between weight percent of the metals. Considering that each metal source acts as nuclei for soot formation and would further enhance the catalytic oxidation of soot, it suggests that higher concentration of metals present in the soot samples would lead to higher activity, which is evident in the values of $T_{\max,\mathrm{DTG}}$ and kinetic parameters for Fe. This is also accompanied by the relatively smaller size of the soot particles in the presence of Fe that was observed from the SEM micrographs. The average particle size of the soot in the presence of Fe is 45 nm, which is lower than those for Ce (52 nm) and Cu (47 nm). The same explanation is also valid when the concentration of each metal source increases; more soot nuclei are present. The changes in kinetic and thermodynamic parameters versus concentration for each metal source are presented in Figure 5.

3.3. Effect of FBCs on CO emission

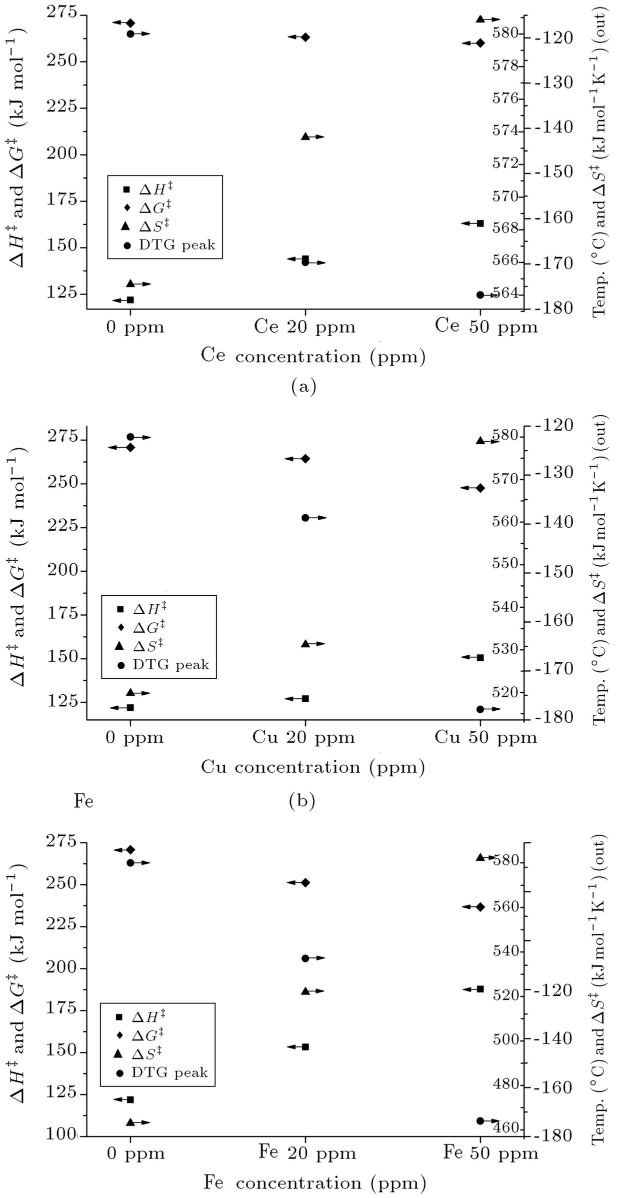
In order to indicate that FBCs favor CO_2 formation in the course of diesel soot oxidation, we defined CO selectivity (S_{CO}) as (mole of CO)/(mole of CO + mole of CO_2). The results are presented in Table 8. As evident, the uncatalyzed soot has higher CO selectivity. Thus, FBCs regenerate the DPF with less CO emission into the environment. However, among all types of metal, Fe shows the least CO selectivity. In summary, the presence of metal component in PM improved the combustion by lowering $T_{\mathrm{DTG,max}}$ from 580 to 464°C when iron was used as the metal source. Based on the results, we concluded that the application of FBC is highly effective for improving the PM combustion in conventional DPF systems.

4. Conclusions

The results of this study indicate that by using FBCs, the soot oxidation temperature decreases significantly. Different solid state reaction models were employed. It was observed that a contracting sphere model would be the proper model to express the reaction behavior. This model was used to find the direction of changes in the kinetic and thermodynamic parameters upon addition of metal complexes to diesel fuel. It was shown that the activation energy of the soot oxidation increases upon addition of a metal complex to the diesel fuel, while, by a decrease in the activation Gibbs free energy, the process becomes less endergonic. It was also shown that by using FBCs, much less CO would be emitted during regeneration of the diesel particulate filter. In comparison, the presence of $Fe(C_8H_{15}O_2)_3$

Table 7. Energy dispersive spectrometry results for the soot obtained from diesel fuel containing 50 ppm metal complexes.

Metal (50 ppm) in diesel	Weight percent of metal in the soot
Ce	0.09
Cu	0.67
Fe	2.58



(a)

(b)

(c)

Figure 5. Kinetic and thermodynamic parameters of the soot samples at different concentration of metal in the diesel fuel derived from contracting sphere model: (a) Ce; (b) Cu; and (c) Fe.

Table 8. CO selectivity obtained from TPO tests on the soot collected from oxidation of diesel containing different concentration of metals.

Selectivity	0 ppm	Ce 20 ppm	Ce 50 ppm	Cu 20 ppm	Cu 50 ppm	Fe 20 ppm	Fe 50 ppm
of CO	32.13	28.69	29.62	27.17	27.39	25.71	20.73

in the diesel fuel facilitates the conditions for soot oxidation significantly, i.e. enabling the soot to be oxidized (similar to self-regeneration of filter) at the average temperature of the exhaust gases. Considering the environmental regulations, Fe seems to be the most suitable source of metal complex to be used as a FBC.

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Biographies

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