Catalysis Today 157 (2010) 432–435

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

The enhancement of low-temperature combustion of diesel PM through concerted application of FBC and perovskite

Dae-Won Lee [a], Ju Young Sung [b], Jai Hyun Park [b], Yoon-Ki Hong [b],
Seong Ho Lee [c], Seung-Hoon Oh [c], Kwan-Young Lee [b,*]

[a] Research Institute of Clean Chemical Engineering Systems, Korea University, 5-1, Anam-dong, Sungbuk-gu, Seoul 136-701, South Korea
[b] Department of Chemical and Biological Engineering, Korea University, 5-1, Anam-dong, Sungbuk-gu, Seoul 136-701, South Korea
[c] Institute of Technology, SK Energy, 14-1, Wonchon-dong, Yuseong-gu, Daejeon 305-712, South Korea

ARTICLE INFO

Article history:
Available online 27 March 2010

Keywords:
Particulate matter
DePM
Diesel particulate filter
Fuel-borne catalyst
Perovskite

ABSTRACT

In this study, we attempted to improve diesel particulate matter (PM) combustion by the simultaneous application of a fuel-born catalyst and a perovskite catalyst. The experiment was simulated by mixing fuel-borne catalyst (FBC)-incorporated PM with perovskite catalyst in a physical manner. FBC-incorporated PM was achieved satisfactorily using a self-constructed PM generator. Through temperature-programmed oxidation (TPO), the catalyst combination of Fe/Ce FBC and $La_{0.7}K_{0.3}FeO_3$ effectively improved the low-temperature combustion of diesel PM, with superior performance to that of the Fe/Ce FBC–Pt/Al_2O_3 combination.

1. Introduction

Low particulate matter (PM) emission is essential for any commercial diesel engine vehicle. With the ongoing intensification of emission regulations, more dedicated tools for engine design and control have been developed and applied to reduce PM emissions from diesel engines. However, the impossibility of complete removal of PM emissions from the engine necessitates the installation of after treatment systems to satisfy the strengthening regulations for diesel emission.

The commercialized diesel DePM technologies commonly use a diesel particulate filter (DPF) to capture and collect PM in the exhaust. The technologies are categorized based on how to burn out the collected PM in the DPF. Among the DePM technologies, fuel-borne catalyst (FBC) and continuous regeneration trap (CRT) prevail throughout the worldwide market. FBC is a fuel additive containing active metals (usually Fe, Ce, Cu, Sr and precious metals) as major ingredients [1], which enhances the fuel combustion in the engine cylinder toward complete oxidation and improves the fuel penalty by decreasing PM emissions. The active metals are finally distributed over PM structure and accelerate the combustion of PM on the DPF. CRT utilizes an oxidation catalyst to convert NO into NO_2, which oxidizes carbonaceous particles much faster and at lower temperature (usually from ~250 °C) than oxygen [2,3]. The oxidation catalyst is positioned before DPF in monolith form and its catalytic components are usually coated on the inner wall of DPF. The active component of the catalyst is usually platinum. The DPF technologies have been well reviewed in terms of catalysis in the literatures [4,5].

However, the DePM technologies are facing a new technological challenge. In CRT, NO_2 starts to combust PM from 250 °C theoretically, although real combustion starts from between 250 and 300 °C in actual engine/vehicle applications. Below 300 °C, the accumulation rate of PM is faster than its combustion rate, which increases the PM trapped on the DPF. If combustion starts at this state, the accumulated PM is combusted at once and excessive heat is released on the DPF, leading to thermal destruction of the DPF structure. The failure of DPF due to excessive burning of PM becomes more critical when a DPF system is applied to the retrofitting of decrepit vehicles. The imbalance between accumulation and combustion of PM at low-temperature is a common threat to all the DePM systems utilizing DPF. This is partially solved by the application of active means such as an onboard heater to heat up the exhaust gas, but such active strategies are only feasible in limited cases where sufficient electricity is available to power the heater. Therefore, the combustive performance on the catalyst-coated DPF must be improved to overcome this challenge.

In this study, we simultaneously applied FBC and perovskite catalyst together to improve the low-temperature combustion rate of PM on DPF. Although perovskite catalysts have been studied for diesel DePM extensively [6–11], the concerted application of FBC and perovskite catalyst has not, to the best of our knowledge, been reported yet. However, several studies on double application have reported mixing the supported platinum catalysts with metal-

---

* Corresponding author. Tel.: +82 2 3290 3299; fax: +82 2 926 6102.
E-mail address: kylee@korea.ac.kr (K.-Y. Lee).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.02.047

activated PM [12,13]. We simulated the concerted application of FBC and perovskite so that FBC-activated PM was combusted on the perovskite catalyst. We incorporated FBC into the PM network by combusting FBC-blended diesel fuel through our self-constructed PM generator. The combustion tests were performed through lab-scale experiments based on temperature-programmed oxidation (TPO).

2. Experimental

PM samples were generated by a self-constructed PM generator utilizing a diesel burner. The air-to-fuel ratio of the diesel burner was tuned to produce a reasonable amount of PM. The air flow rate was adjusted to 0.15 m^3/min and the fuel injection rate to 3.86 l/h. The fuel was Ultra-Low Sulfur Diesel (ULSD) containing sulfur at less than 15 ppm. The FBC was DPX-10 from Rhodia which contains cerium and iron as the active metal species. The FBC was blended with ULSD at a ratio so that 100 ppm of cerium was finally dissolved in the FBC–ULSD mixture. The PM samples from the FBC–ULSD fueled PM generator were designated as "FBC PM", those from pure ULSD as "Plain PM", and those from a real diesel bus engine (12L) using the plain ULSD as "Engine PM". The elemental compositions and particle size distributions of the PM samples were determined using an elemental analyzer (Flash EA 1112, CE Inst.) and a transmission electron microscope (TEM; Tecnai 20, Fei Co.) respectively. After preserving PM samples in the constant relative humidity (45%) and temperature (22 °C) for 24 h, the content of soluble organic fraction (SOF) was measured through Soxhlet extraction using dichloromethane as a solvent.

The 5 wt.% Pt/Al_2O_3 catalyst was prepared through incipient wetness method using $H_2Cl_6Pt{\cdot}6H_2O$ as a precursor for Pt. The perovskite catalysts were prepared following the method reported in the literature [7]. Initially, $La_{1-x}K_xFeO_3$ catalyst was chosen as test catalyst because it showed the best performance for combustion of pure carbon (Printex-U) in our previous study [8]. All the perovskite catalysts showed BET areas of 4–6 m^2/g. After proper X-ray diffraction (XRD) measurement, only the pure perovskites without trace oxides were selected as test catalysts. (Fig. 1 shows the pure perovskite structures of tested catalysts.)

The combustion test followed the TPO procedure. PM (40 mg), catalyst (18 mg) and SiC (400 mg) were mixed under an agar mortar for 15 min, and the mixture was packed in the middle of a glass tubular reactor (I.D. = 9.6 mm). The TPO was conducted as the temperature of the packed bed was increased from 250 to 700 °C at a ramp rate of 1 °C/min. The gas flow consisted of NO (500 ppmv), O_2 (8 vol.%) and He (balance), which was fed into the reactor at a volumetric flow rate of 100 mL/min (GHSV = 10,453/h).

3. Results and discussion

First, the eligibility of the PM samples as test PM was evaluated. The properties of the PM samples were measured via TEM, Soxhlet extraction and elemental analysis, those results are listed in Table 1. The Plain PM from the PM generator exhibited a larger average size, and lower oxygen and SOF contents than the real Engine PM, implying that the combustibility of the former was inferior to that of the latter. Comparing the results of Plain and FBC PM, the application of FBC resulted in a smaller particle size and lower SOF content. This result suggested that FBC worked properly on the PM generation in the PM generator. The concentrations of metallic species contained in the FBC PM were 1.45 wt.% for Fe and 0.14 wt.% for Ce. The species were highly dispersed in the PM structures, as demonstrated by the absence of any detectable metallic agglomerates in the TEM/HR-TEM images (Fig. 2). The tissues observed in the images are PM particles, which are similar to the images elsewhere [14].

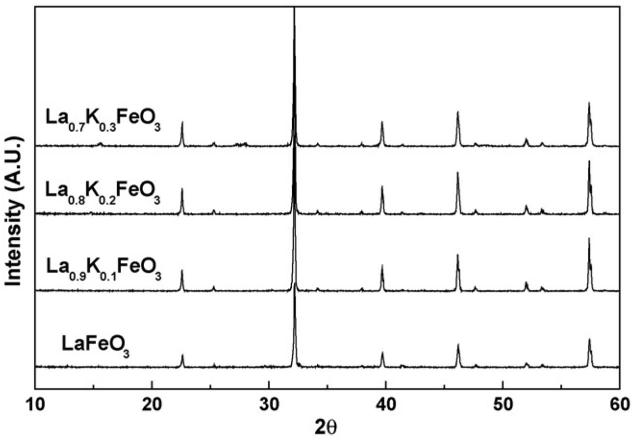

Fig. 1. XRD results of $LaFeO_3$ and $La_{1-x}K_xFeO_3$ (x = 0.1, 0.2, 0.3) catalysts.

These dimensional and compositional features of the PM samples were reflected in the TPO results of PM only (Fig. 3). The Engine PM started to burn at 430 °C while Plain PM did at higher temperature of 490 °C, which was in line with our expectation for the combustibilities based on the PM properties. Therefore, the evaluation of combustion catalyst using PM sample from PM generator is expected to be conservative.

When the FBC PM was tested, the TPO profile was positioned at a lower temperature region than that of the Plain PM, clearly demonstrating the positive effect of FBC on the PM combustibility.

Based on these results, we concluded that the PM samples from the self-constructed PM generator were eligible as test PMs for further study, because the self-constructed PM generator produced PM samples similar to those of the real engine PM while avoiding any unwanted improving effects on the combustibility. The effective incorporation of FBC into the PM network was another factor ensuring the eligibility of the PM generator.

Fig. 4 shows the TPO results of the PM samples both with and without the combustion catalysts (Pt/Al_2O_3 and $La_{0.7}K_{0.3}FeO_3$). The PM combustion rate was replaced by the CO_2 flow rate from the reactor outlet, as CO was not detected in any of the tests. All the TPO results showed peak-type profiles, with decreasing PM amount as TPO continued, which induced a kinetic reduction point in the combustion rate. The performance was evaluated by the ignition

Table 1
Average particle sizes, SOF and elemental contents of Engine PM, Plain PM and FBC PM.

Sample	Average size (nm)[a]	SOF content (%)[b]	Elemental concentration (%)[c]			
			C	H	O	Others
Engine PM (*from 12L Engine*)	68.5	31.9	82.40	0.46	9.15	7.99
Plain PM (*from PM Generator*)	75.0	26.9	86.21	0.35	4.79	8.65
FBC PM (*from PM Generator*)	68.9	24.7	86.62	0.46	6.60	6.32

[a] Average value determined by TEM analysis.
[b] Calculated based on the change of PM mass following Soxhlet extraction.
[c] Calculated through elemental analysis.

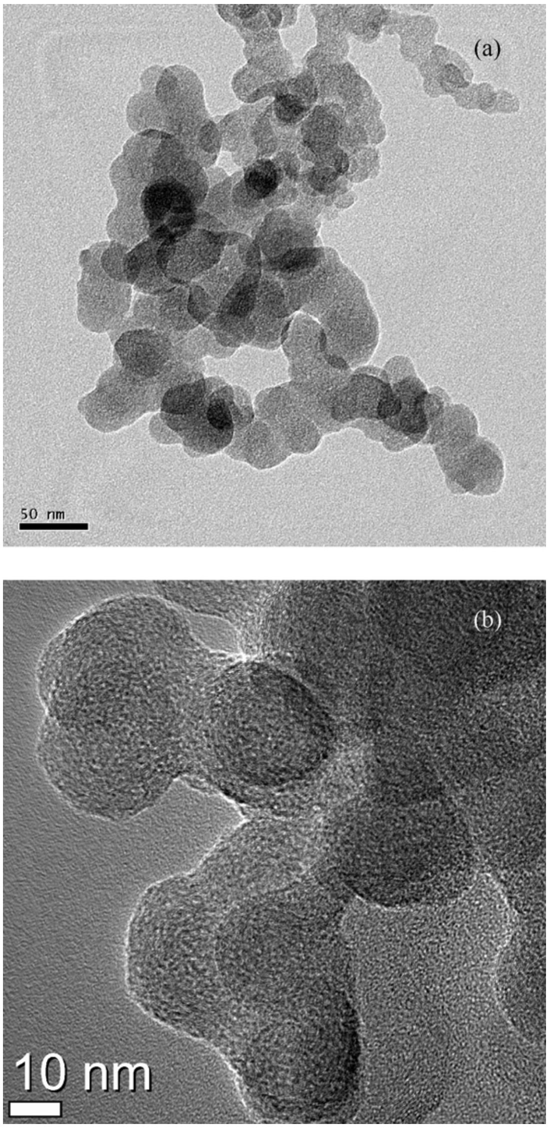

Fig. 2. (a) TEM (150,000×) and (b) HR-TEM (600,000×) images of FBC PM.

(T_{ig}, the temperature when the first CO_2 flow was detected) and max (T_{max}, the temperature at max CO_2 flow rate) temperatures. T_{ig} and T_{max} are listed for each case in Table 2. The max CO_2 flow rate was not considered for the evaluation, because it may have presented a relatively lower value when the combustion rates were faster at temperatures below T_{max}. This was demonstrated by the comparison between the TPO results for Plain PM and FBC PM. T_{ig} and T_{max} for FBC PM (470 and 530 °C, respectively) were lower than those of Plain PM (490 and 570 °C). However, the max CO_2 flow rate of the former was less than that of the latter (1.1 and 1.4 mL/min, respectively), which was attributed to the difference between the two cases in the combustion rates before reaching T_{max}.

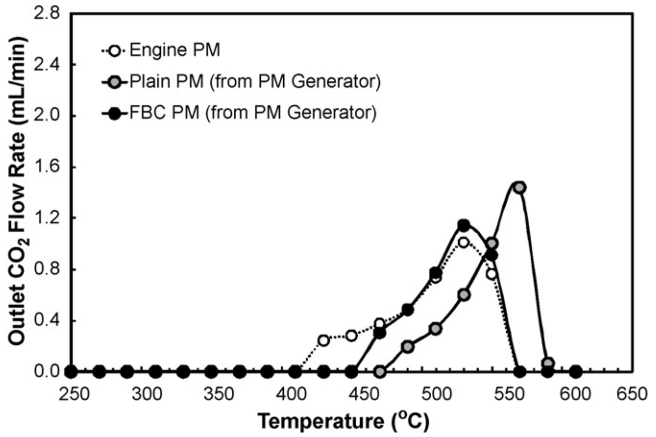

Fig. 3. TPO results for Engine PM, Plain PM and FBC PM (without powder catalyst).

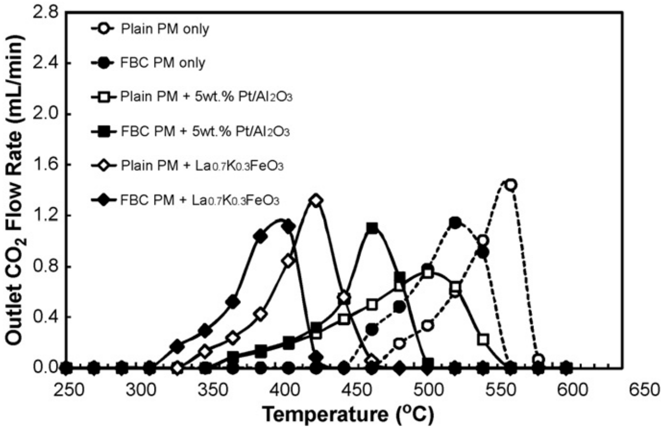

Fig. 4. TPO results for Plain PM and FBC PM mixed with 5 wt.% Pt/Al_2O_3 and $La_{0.7}K_{0.3}FeO_3$.

The introduction of the combustion catalyst definitely enhanced the combustion rate in each case. When Pt/Al_2O_3 was mixed with PM, T_{ig} was lowered by more than 100 °C from each PM-only case. The presence of FBC component in the PM network improved the low-temperature combustion, lowering T_{max} from 510 to 470 °C. However, T_{ig} did not change (370 °C) when Plain PM was replaced by FBC PM in the presence of Pt/Al_2O_3. Mixing PM with perovskite catalysts resulted in a similar pattern of improvement, but with more prominent decreases of T_{ig} and T_{max}. When FBC PM was mixed with $La_{0.7}K_{0.3}FeO_3$ catalyst, T_{ig} was decreased to 330 °C and T_{max} to as low as 410 °C, which was lower 60–100 °C than that for the Pt/Al_2O_3 catalysts. The combustion was terminated before 450 °C, where FBC PM, in the absence of any combustion catalyst, cannot undergo self-ignition. The CO_2 flow rates afforded by 'FBC PM + $La_{0.7}K_{0.3}FeO_3$' before T_{max} (410 °C) were 5–7 times larger than those afforded by 'Plain PM + 5 wt.% Pt/Al_2O_3' or 'FBC PM + 5 wt.% Pt/Al_2O_3'. Based on the assumption that these two latter set-ups represented rough models of commercial CRT and FBC–DPF, we concluded that the concerted application of FBC and $La_{0.7}K_{0.3}FeO_3$ is very effective for improving the low-temperature PM combustion of conventional, catalyst-driven DPF systems.

It is noteworthy that such improvements were found even in the relatively unfavorable conditions of low catalyst/PM weight ratio (0.45) and excessive amount of heat absorber (SiC), both of which drastically reduce the possibility of contact between PM and catalyst.

The improvement of performance was definitely dependent on the elemental composition of the perovskite catalyst. The

Table 2
Ignition temperature (T_{ig}) and max temperature (T_{max}) for each TPO case in Fig. 4.

Case	Ignition temperature (T_{ig}, °C)	Max temperature (T_{max}, °C)
Plain PM only	490	570
FBC PM only	470	530
Plain PM + 5 wt.% Pt/Al_2O_3	370	510
FBC PM + 5 wt.% Pt/Al_2O_3	370	470
Plain PM + $La_{0.7}K_{0.3}FeO_3$	350	430
FBC PM + $La_{0.7}K_{0.3}FeO_3$	330	410

partial substitution of an A-site element (usually La) with potassium remained effective, although the conventional soot materials reported in the literature [6–8] were replaced by FBC PM in this study. The choice of the B-site element also strongly affected the combustion performance. The best result was obtained with $La_{0.7}K_{0.3}FeO_3$, but further testing is off the ground and further improvements are expected in the future. Concurrently, we are also investigating the synergistic effect from the combination of FBC and perovskite. We consider it likely that the FBC component (Fe and Ce) either helps to create the CC–O complex (decomposed then into active carbon sites) on the carbon surface [14] or catalyzes the activation of NO into the surface nitrates on the perovskite catalyst [9].

4. Conclusion

In an alternative approach, PM samples were obtained in a state similar to that produced by diesel automotive engines, by correct adjustment of the A/F ratio of the diesel burner. The concerted application of Fe/Ce FBC and perovskite ($La_{0.7}K_{0.3}FeO_3$) was effective in enhancing the low-temperature combustion of diesel PM. This combination advanced T_{max} by 60–100 °C, compared with the combustion results afforded by Pt/Al_2O_3, which is widely used as a PM-burning catalyst in commercialized DPF technologies. The investigation of catalytic interaction between FBC and perovskite is on the progress now. Also, evaluation of catalyst system on the engine bench is expected to follow in the near future.

Acknowledgement

The authors gratefully acknowledge the financial support for this work provided by SK Energy under the BK21 program of the Ministry of Education, Science and Technology, South Korea.

References

[1] Dieselnet: Filter with fuel additives, http://www.dieselnet.com/tech/dpf_add.html.
[2] Dieselnet: Diesel filter regeneration, http://www.dieselnet.com/tech/dpf_regen.html.
[3] B.J. Cooper, J. Thoss, SAE Technical Paper 890404 (1989) 171.
[4] B. van Setten, M. Makkee, J.A. Moulijn, Catal. Rev. 43 (2001) 489.
[5] M.V. Twigg, Appl. Catal. B: Env. 70 (2007) 2.
[6] Y. Teraoka, S. Kagawa, Catal. Sur. Jpn. 2 (1998) 155.
[7] Y. Teraoka, K. Kanada, S. Kagawa, Appl. Catal. B: Env. 34 (2001) 73.
[8] D.-W. Lee, S.-J. Song, K.-Y. Lee, Korean. J. Chem. Eng. 27 (2010) 452.
[9] D. Fino, P. Fino, G. Saracco, V. Specchia, Appl. Catal. B: Env. 43 (2003) 243.
[10] D. Fino, P. Fino, G. Saracco, V. Specchia, Chem. Eng. Sci. 58 (2003) 951.
[11] J. Liu, Z. Zhao, C. Xu, A. Duan, Appl. Catal. B: Env. 78 (2008) 61.
[12] S.J. Jelles, R.R. Krul, M. Makkee, J.A. Moulijn, Catal. Today 53 (1999) 623.
[13] S.J. Jelles, M. Makkee, J.A. Moulijn, G.J.K. Acres and J. D. Peter-Hoblyn, SAE Technical Paper 1999-01-0113 (1999) 1.
[14] W. Dreher, A. Harscher, W. Nisch, C. Burkhardt, Proceedings of the 6th ETH Conference on Nanoparticle Measurement, Zurich, 2002;
D. Reichert, H. Bockhorn, S. Kureti, Appl. Catal. B: Env. 80 (2008) 248.