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Kinetic Study on Soot Oxidation by Simulated Diesel Gas Emissions

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Overview

- Introduction
- Relevance and Objectives
- Experimental
- Theory of Analytic Methodologies
- Results
 - Activation energies according to different methodologies
 - NO_x , O_2 , and CO_2 effects on soot oxidation behaviors
 - Activation energies according to different NO_2 concentration
- Summary
- Acknowledgements

Introduction

■ Development of Advanced DPF systems

- Deeper understanding about filtration and regeneration mechanisms is necessary.
- Thermal runaway during DPF regeneration is a potential problem.
- Therefore, the accurate evaluation of kinetic parameters and soot oxidation behaviors is required. (SAE 2010-01-2166)
- Modifications of channel structures and geometry have also been studied. (SAE 2010-01-0537).

Relevance and Objectives

- Activation energy of soot oxidation has been evaluated to be different, depending on experimental conditions, instruments used, and analytic methodologies.
- Kinetic parameters of soot oxidation need to be evaluated at the same emissions compositions as those in engine emissions, including NO_x , O_2 and CO_2 .
- Assess the activation energy of soot oxidation at different oxidation conditions and various analytic methodologies to obtain its most accurate values.
- Evaluate soot oxidation behaviors and kinetic parameters at the ambient experimental conditions simulating real engine emissions, consisting of NO_x , O_2 and CO_2 .

Experimental

■ Sample materials

- Carbon black (Printex-U)

■ Instruments

- Thermogravimetric analyzer (TGA)

■ Evaluation of the effects of inert gases and analytic methodologies

- Reactant gas mixture: 40% (He, N₂ and Ar) + 60% air
- Analytic methodologies
 - Isothermal kinetic analyses: 575°C, 600°C, 625°C
 - Non-isothermal kinetic analyses (various heating rates at 1 – 10 °C/min)
 - Integral method
 - Iso-conversional method
 - Differential method

■ Evaluation of kinetic parameters with various compositions of reactant gases (See table)

Experimental (Cont'd)

- Various compositions of reactant gases have been used to evaluate kinetic parameters at diesel emissions conditions.

No	Concentrations of reactant gases			
	NO (ppm)	NO ₂ (ppm)	CO ₂ (%)	O ₂ (%)
1	0	0	<u>8</u>	0
2	0	0	8	<u>8</u>
3	<u>225</u>	0	8	0
4	<u>1000</u>	0	0	0
5	0	225	8	<u>0</u>
6	0	225	8	<u>4</u>
7	0	225	8	<u>8</u>
8	0	225	<u>0</u>	8
9	0	<u>180</u>	3.5	13.5
10	0	<u>450</u>	8	8
11	0	<u>1250</u>	10	5.5

Theory of the different analytic methodologies

■ Isothermal kinetic analysis

- $\alpha = \frac{m_0 - m}{m_0 - m_1}$ (Degree of conversion)
- $\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha)$ (Rate of reaction)
- $f(\alpha) = (1 - \alpha)^n$ (Simplified kinetic expression)
- By taking logarithm, $\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E_a}{RT} + \ln(A) + n(1 - \alpha)$ ($\ln\left(\frac{d\alpha}{dt}\right)$ vs. $\frac{1}{T}$)

■ Non-isothermal kinetic analysis

- $\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha)$ ($\beta = \frac{dT}{dt}$: heating rate)
- $\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_{T_0}^T \left[\frac{A}{\beta} \cdot \exp\left(-\frac{E_a}{RT}\right)\right] dT$
- Integral method
 - $g(\alpha) = \frac{A}{\beta} \cdot \frac{E_a}{R} \cdot p(x)$ [$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$, $p(x) = \int_x^\infty \frac{e^{-u}}{u^2} du$, $u = \frac{E_a}{RT}$]
 - Coats-Redfern's approximation, $p(x) = e^{-x} \frac{x-2}{x^2}$
 - By taking logarithm, $\log \frac{g(\alpha)}{T^2} = \log \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right) \right] - \frac{E_a}{2.3RT}$ ($\log \frac{g(\alpha)}{T^2}$ vs. $\frac{1}{T}$)

Theory (cont'd)

➤ Iso-conversional method (Vyazovkin)

- $g(\alpha) = \frac{A}{\beta} \cdot \frac{E_a}{R} \cdot p(x)$

- Different heating rates $[\beta_i (i = 1, \dots, n)]$

- Approximation: $p(x) = \frac{e^{-x}}{x} \cdot \frac{x^2 + 10x + 18}{x^3 + 12x^2 + 36x + 24}$, where $x = \frac{E_a}{RT}$

➤ Differential method

- $\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot (1 - \alpha)^n$

- By taking logarithm, $\log\left(\frac{d\alpha}{dt}\right) - n \log(1 - \alpha) = -\frac{E_a}{RT} + \log A$,

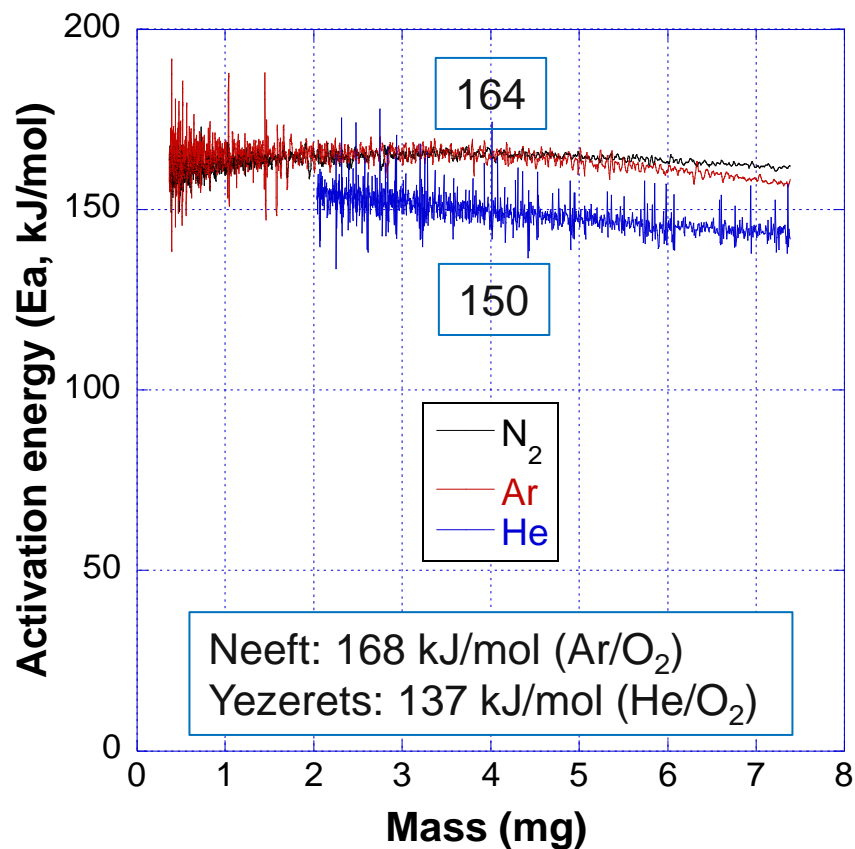
$\log\left(\frac{d\alpha}{dt}\right) - n \log(1 - \alpha)$ vs. $\frac{1}{T}$ for hypothesized n

Results – Part 1

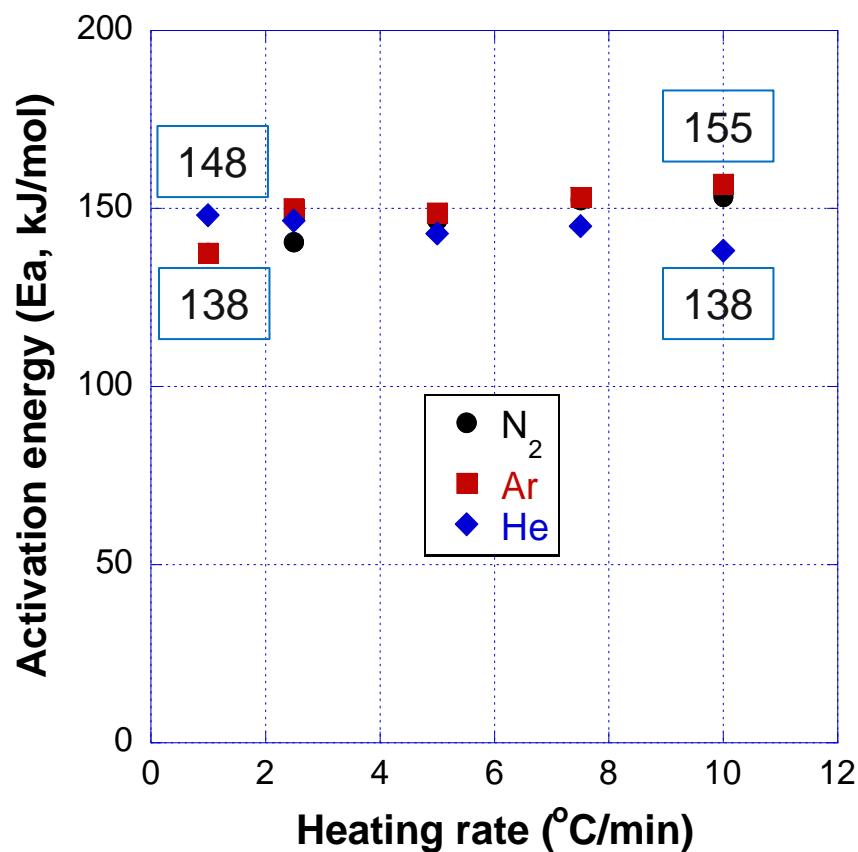
- Effects of inert gas and analytic methodologies
 - **Isothermal experiments:**
 - Effects of inert gas on activation energy
 - **Non-isothermal experiments:**
 - Effects of Inert gas and heating rate on activation energy

Activation energy is quite dependent on inert gas and heating rate

➤ Isothermal kinetic analysis

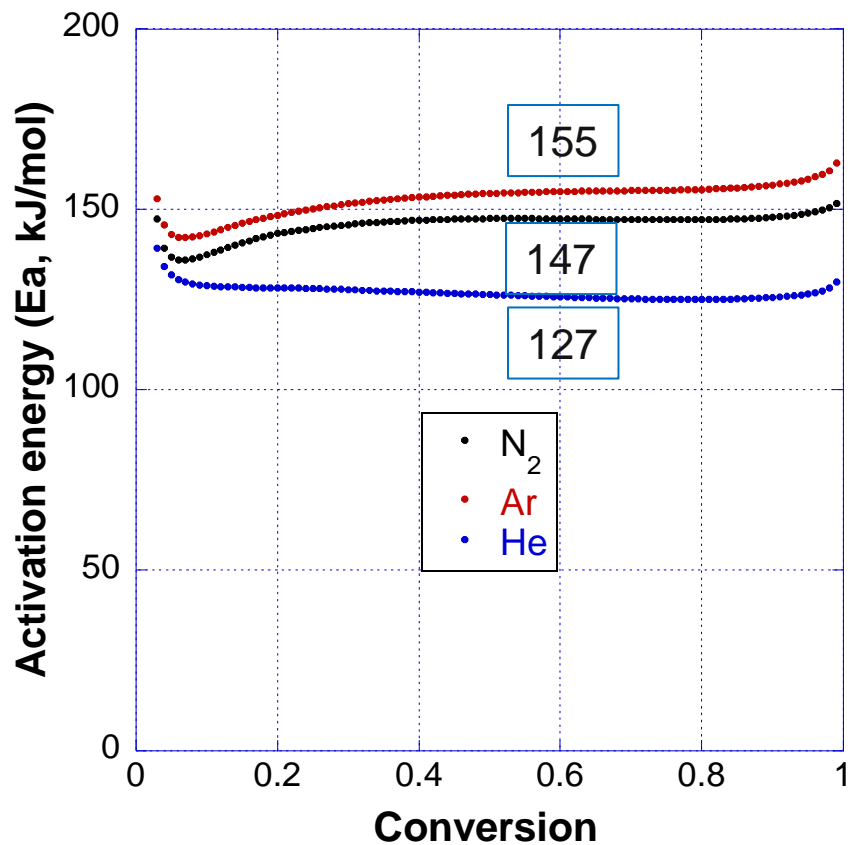


➤ Non-isothermal: Integral method

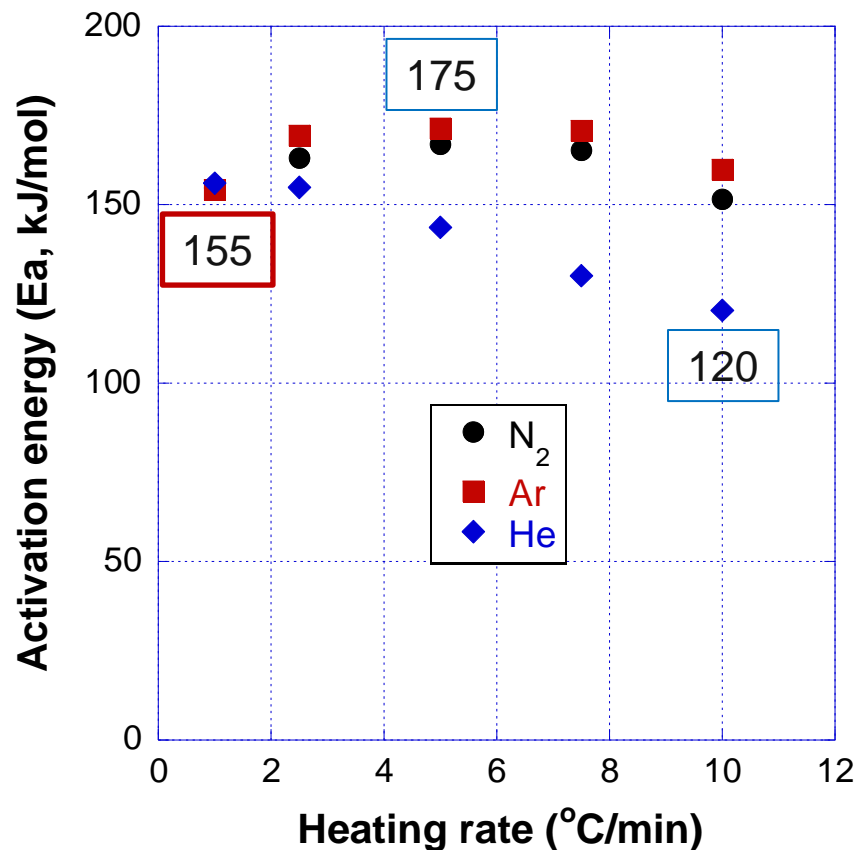


Differential method proposed an activation energy independent of inert gas at the heating rate of 1°C/min

➤ Non-isothermal:
Iso-conversional method



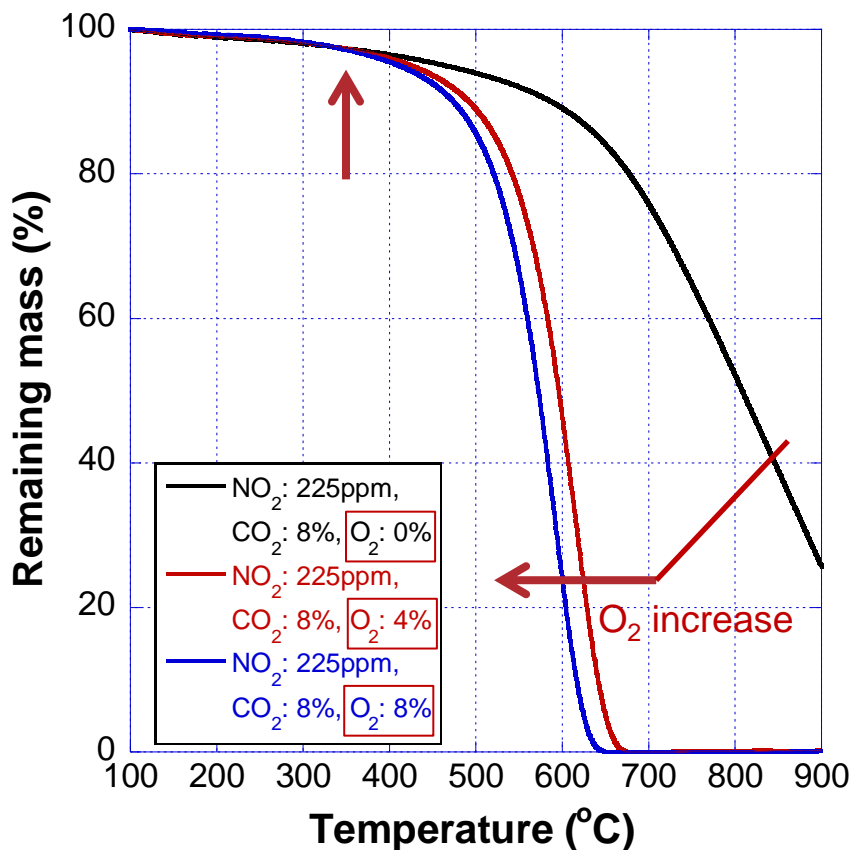
➤ Non-Isothermal:
Differential method



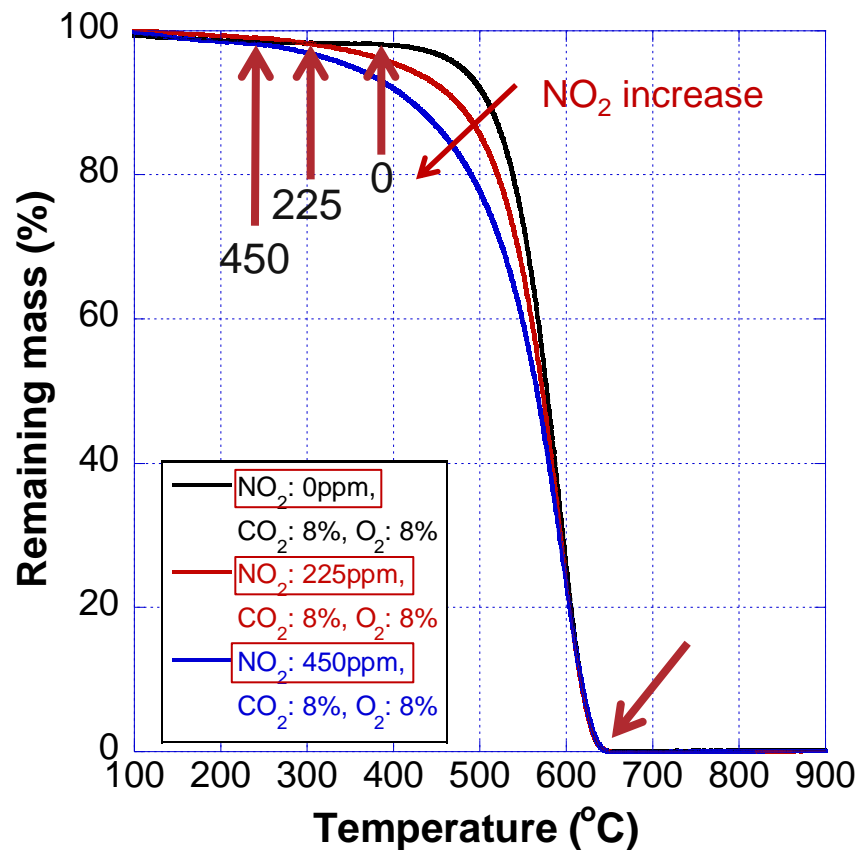
Results – Part 2

- Examination of soot oxidation behaviors for various reactant gas compositions
 - Non-isothermal experiments with 1°C/min of heating rate (Instantaneous mass vs. Temperature)
 - Analytic methodology: Differential method

NO_2 promotes soot oxidation at low temperatures, while O_2 does at high temperatures

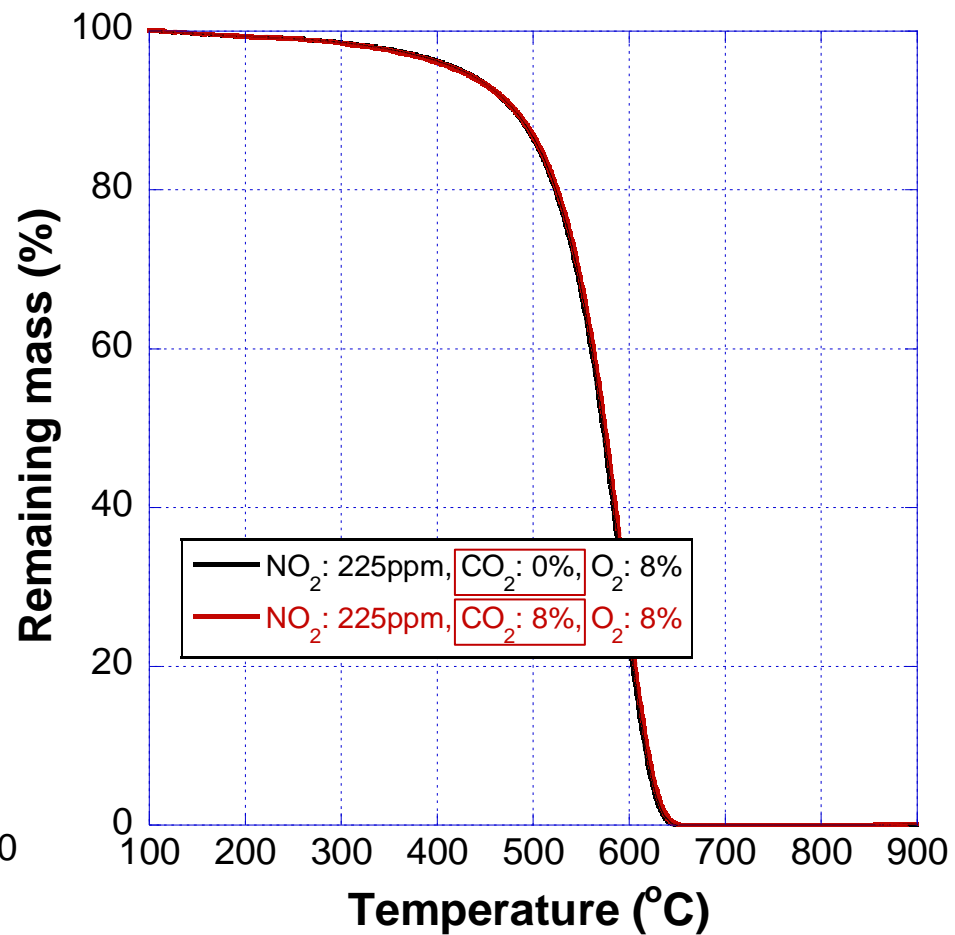
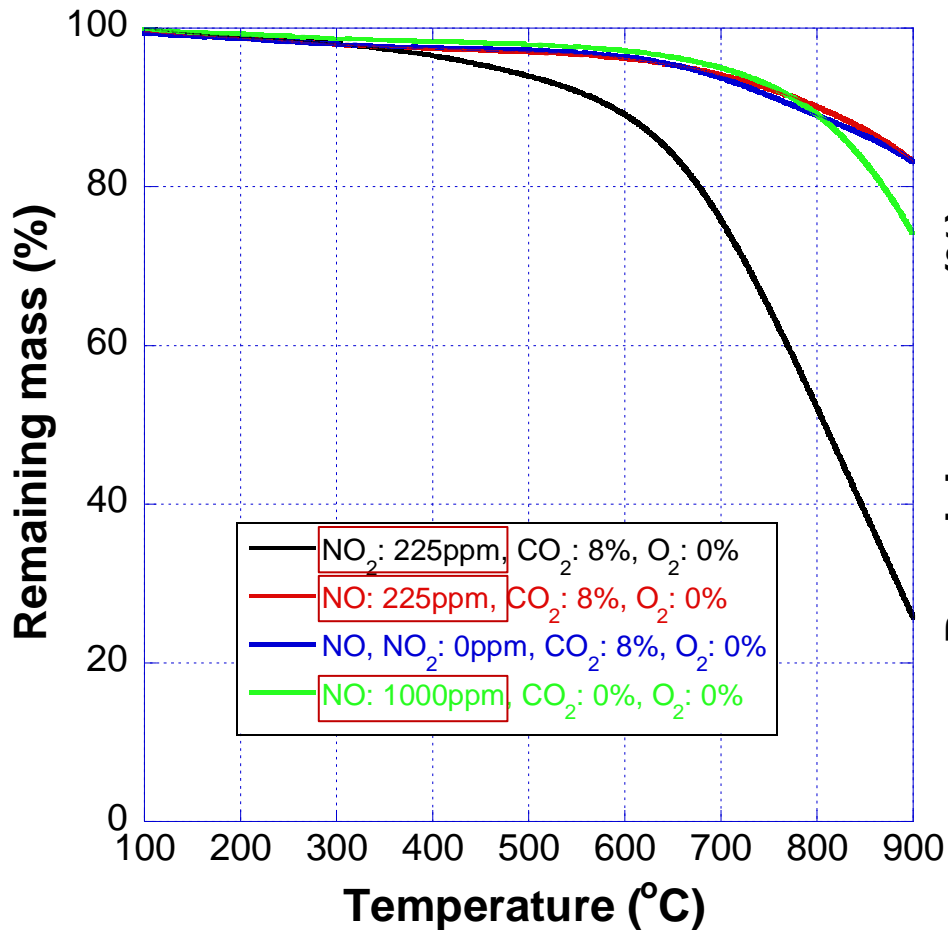


O_2 effects

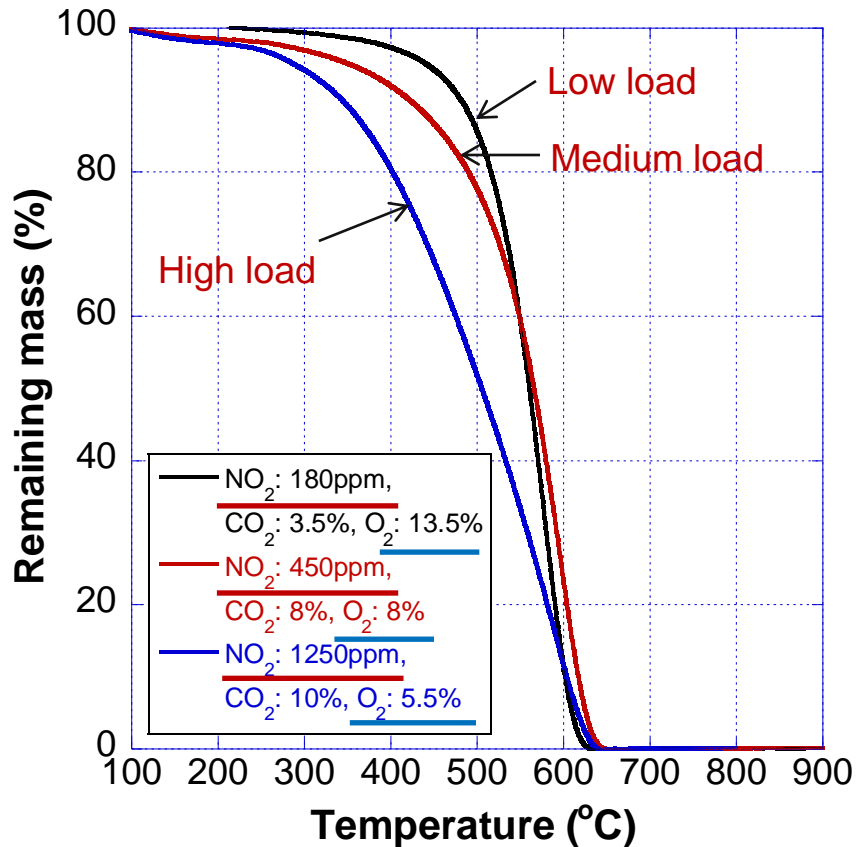


NO_2 effects

NO and CO₂ effects turned out to be minor

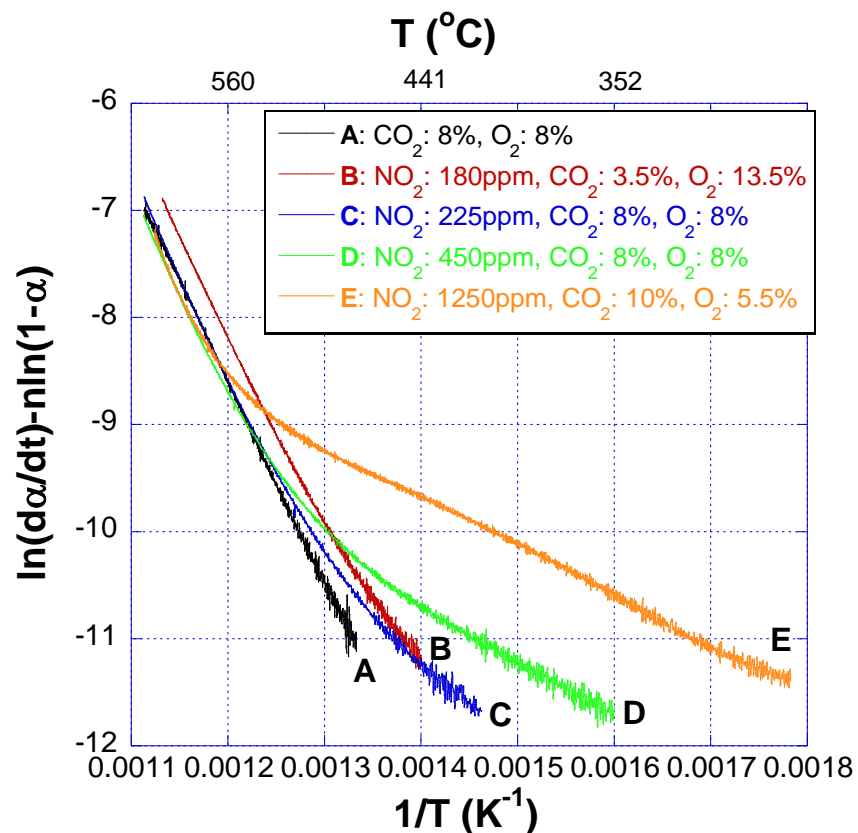


High engine load condition promotes soot oxidation in a wide temperature range by high NO_2 concentration



- **Simulated engine emissions**
 - Hypothesis: NO was fully converted to NO_2 .
- High NO_2 concentration at the high load expanded the oxidation zone to the lower temperature (thermal runaway control)

Arrhenius plots show two explicit oxidation zones in the presence of NO_2

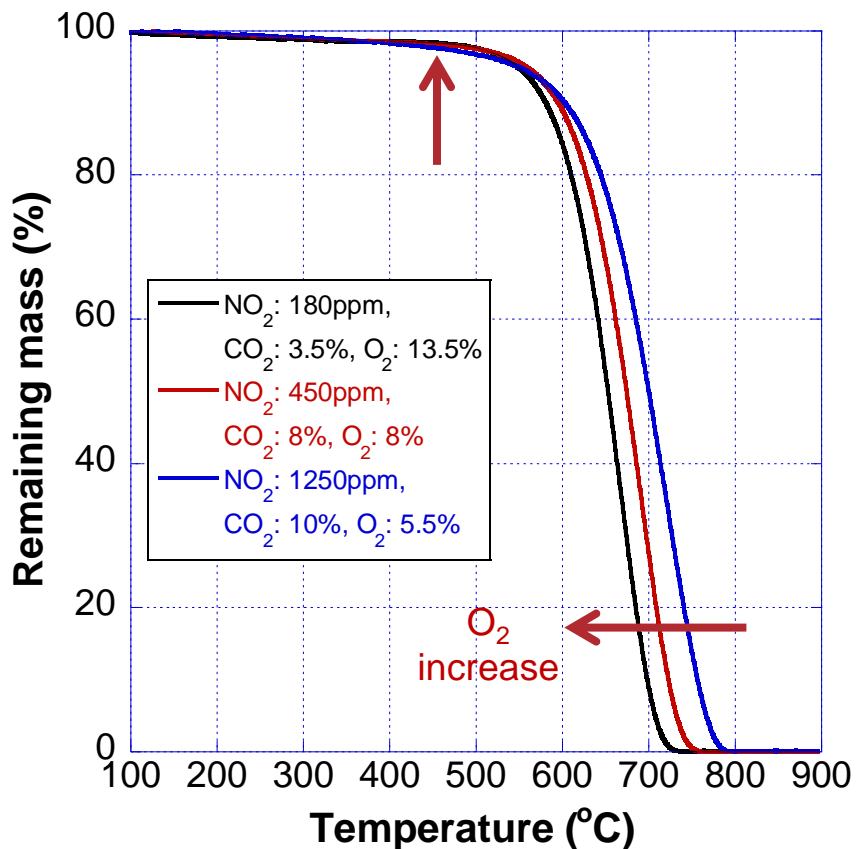


➤ Kinetic analysis

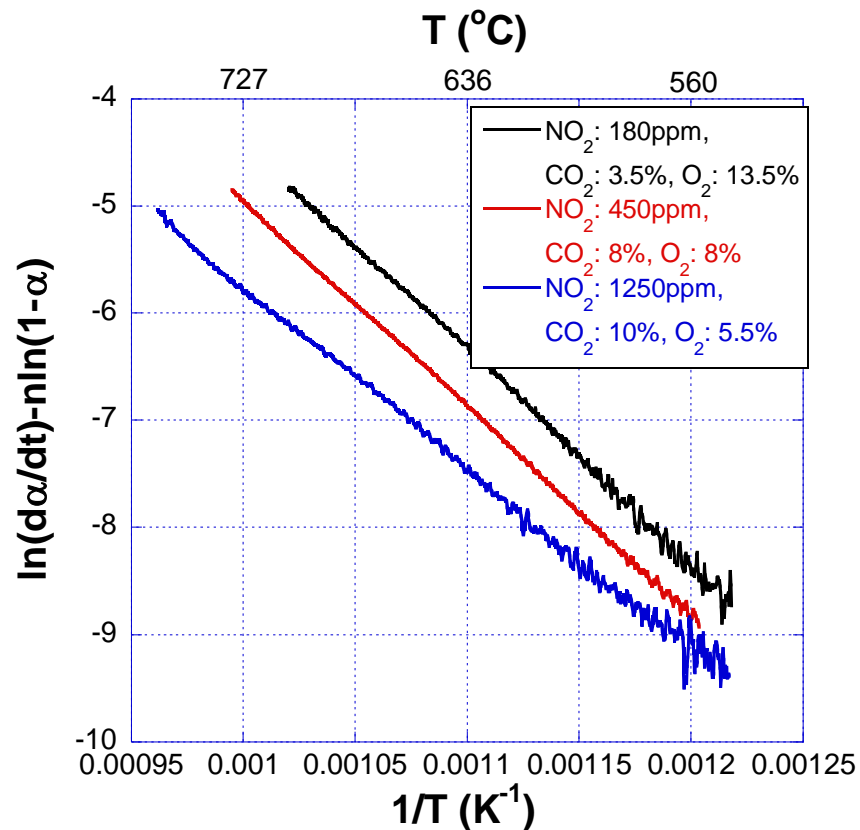
(5 – 95% conversion)

- In presence of NO_2 , two different oxidation behaviors were observed at high and low temperature zones, respectively.
- Increased NO_2 expanded mainly the low-temperature oxidation.
- Therefore, two sets of kinetic parameters (e.g., activation energy, reaction order, etc.) need to be evaluated for each condition.

However, the use of a high heating rate does not show the NO₂ effects clearly

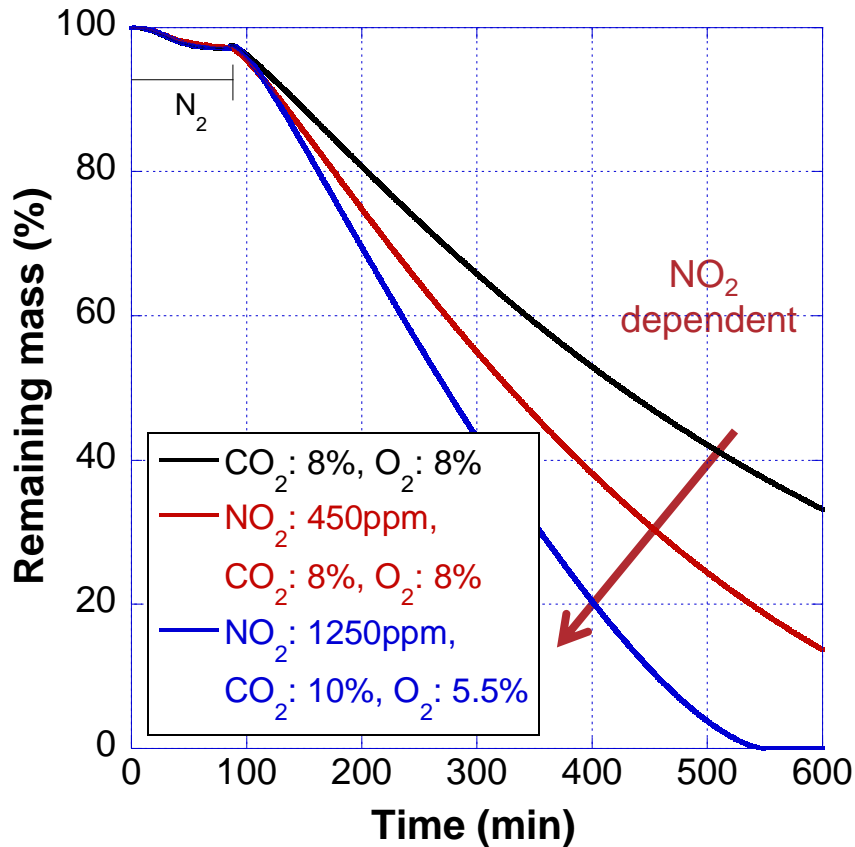


Non-isothermal experiments with 10°C/min

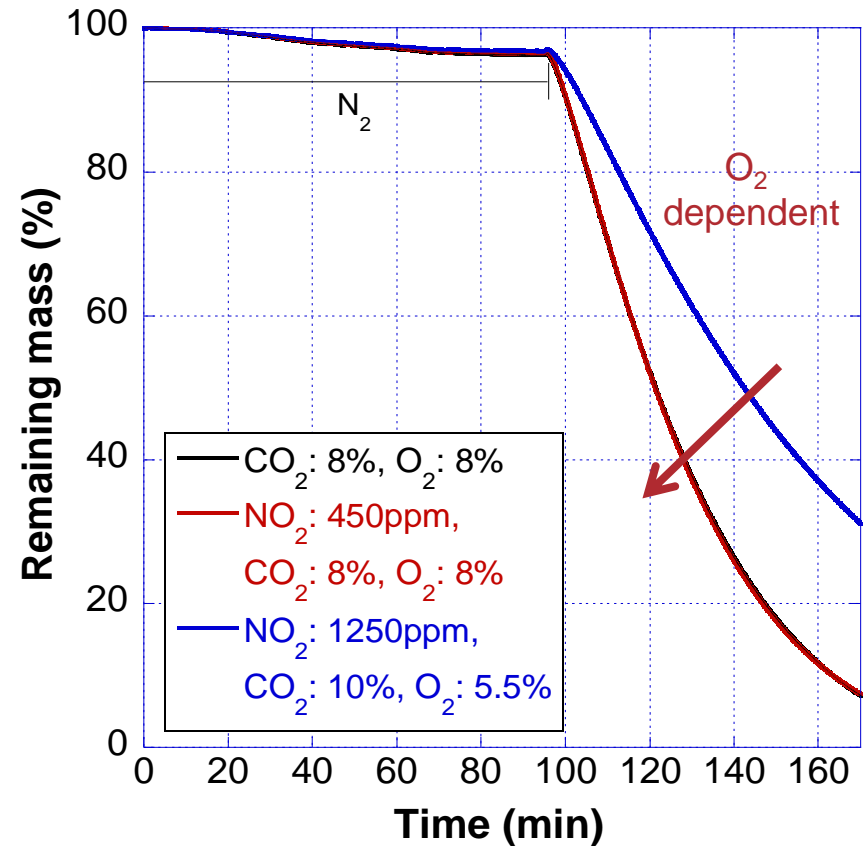


Arrhenius plots with 10°C/min

Isothermal experiments further confirmed the temperature dependence of NO_2 and O_2 oxidation



500°C oxidation



600°C oxidation

Activation energy was evaluated for two oxidation zones (E_a is significantly lower in the LT zone)

Compositions (NO ₂ : ppm, CO ₂ & O ₂ : vol%)	Low temperature (LT) zone			High temperature (HT) zone		
	T (°C)	E _a (kJ/mole)	n	T (°C)	E _a (kJ/mole)	n
a) NO ₂ : 0, CO ₂ : 8, O ₂ : 8	T (°C): 477 – 625, E _a (kJ/mole): 153, n = 0.83					
b) NO ₂ : 180, CO ₂ : 3.5, O ₂ : 13.5	441 – 491	105	1	515 – 610	154	0.85
c) NO ₂ : 225, CO ₂ : 8, O ₂ : 8	410 – 471	67	1	526 – 625	157	0.80
d) NO ₂ : 450, CO ₂ : 8, O ₂ : 8	352 – 471	44	1	550 – 626	154	0.80
e) NO ₂ :1250, CO ₂ : 10, O ₂ : 5.5	288 – 500	39	1	575 – 616	159	0.85

- With increased NO₂ concentration,
 - LT zone: E_a decreased; the LT-zone expanded.
 - HT zone: E_a remained fairly constant.
- The NO₂ effects need to be optimized for efficient soot oxidation in consideration of oxidation temperature.

Summary

- Activation energy was found to be sensitive to inert gas and heating rate.
- The “Differential Method” offered an inert gas-independent activation energy at the heating rate of 1°C/min.
- NO₂ promoted soot oxidation mainly at the low temperature zone, while O₂ did at the high temperature zone.
- Activation energies for soot oxidation were evaluated at two different temperature zones, only when NO₂ was present in gas mixtures.
 - With increased NO₂
 - Low temperature zone: E_a significantly decreased and the LT-zone expanded.
 - High temperature zone: E_a remained fairly constant.
- Both NO₂ concentration and oxidation temperature need to be optimized for effective DPF regeneration.

Acknowledgement

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