Catalytic oxidation of soot in microscale experiments

Martin Seipenbusch and Sheldon K. Friedlander
Chemical Engineering Department University of California Los Angeles

Introduction

Diesel soot from automotive exhaust is a significant constituent of the urban aerosol. Due to the composition of soot particles, a carbonaceous, solid core and adsorbates like polycyclic aromatic hydrocarbons, and their inhalability due to the fine particle size, these particles are cause of concern for public health. To minimize the potential risk, a reduction of the particulate emissions of diesel powered vehicles is sought by means of improved motor technology and by the development of soot traps. On the engine side new technologies have enabled an increase in fuel efficiency and a decrease in overall particulate mass emission. However, to meet future emission standards in the US and Europe, a combination of engine improvement and filter technology is necessary. To enhance the durability of soot traps, the continuous regeneration of the filter element is essential. This is done by the oxidation of the trapped particulate material and is substantially facilitated by the use of catalysts in combination with the soot trap. Many studies have been conducted on the catalytic oxidation of soot, a large number of catalysts and catalyst-support combinations have been addressed. Although a lot of work has been done, the mechanism of the oxidation of soot remains largely unknown. The studies reported in literature so far have been carried out on bulk powder mixtures, an experimental technique that does not allow the definition of the contact between soot and catalyst particles. Purpose of this study was to determine the effects of the particle size of Pt-catalysts and of the inter particle distance between soot and catalyst. Experiments were carried out on a microscopic scale on SiO/SiO_2-coated transmission electron microscope (TEM) grids, laden with Pt particles and soot. The particle size, inter-particle distance and the progress of the reaction were obtained by analysis of TEM- and SEM-micrographs. These experiments on the microscale enabled the correlation between the examined parameters and the reaction rate.

Experimental

To construct a model supported catalyst, platinum nanoparticles and carbon particles were deposited on a SiO_2 layer such that there was loose contact between catalyst and carbon particles, closely resembling the conditions in a soot trap. Carbon black - laden catalytic surfaces prepared in this way were heated at various temperatures and gas compositions in a pre-tempered quartz tube reactor.

In order to obtain information about the interactions between catalyst and carbon in the reactor during oxidation, we used an analysis previously applied by Jung et al. in non-catalytic combustion experiments. SEM and TEM micrographs of single carbon nanoparticle agglomerates were taken before and after they underwent oxidation in the reactor. Changes in the projected area of the carbon agglomerates, induced by the reaction, were monitored using the image analysis software ImageJ developed by the NIH.

Results and Discussion

The reproducibility of the reaction rates determined in our microscale experiments was good, as the comparison between two independently obtained sets of data showed.

Thus the accuracy of the method was shown to be good enough to draw conclusions on the basis of the results.

The oxidation rate of carbon particles showed a linear dependence on the amount of Pt surface area present in the direct surroundings of the carbon particles. This behavior can be explained by making the assumption that the NO_2 concentration is proportional to the catalyst surface area and further, that the rate of carbon oxidation is first order with respect to NO_2. These two assumptions would lead to a linear dependence of the oxidation rate on the Pt surface area, as long as the formation of NO_2 from NO is far from equilibrium.

The variation of the distance between soot and catalyst particles yielded a reciprocal dependence of the rate of reaction on the median distance. This can be interpreted thus, that the oxidation of the carbon particles occurs mainly by NO_2 which is formed on the Pt particles and transported via gas phase diffusion. The concentration of NO_2 from a point source decreases by this function. If the carbon oxidation is first order with respect to NO_2, it's concentration would be proportional to the reaction rate, which thus would show the same dependence on the distance to the NO_2 source.

An effect of the particle size on the rate of oxidation, apart from a positive effect by the increase of the specific surface area, was not discernable. This is surprising, since the oxidation of NO on Pt is reported to be structure sensitive. A decrease of the catalytic activity with decreasing particle size has been reported repeatedly and is mainly attributed to the formation of PtO. Further investigation in this point is thus needed.

It could be observed in the TEM images after reaction, that the number of primary particles changed. This shows that the rate of reaction varies between individual primary particles, so that some disappear completely, while others remain. This combustion behavior of the carbon particles was observed before for uncatalysed reactions in air, and could be linked to anisotropies in soot particles and differing reactivities attributable to specific structural features.

CATALYTIC OXIDATION OF SOOT: INFLUENCE OF INTERPARTICLE DISTANCE AND PARTICLE SIZE ON REACTION RATE

Martin Seipenbusch, Sheldon K. Friedlander

Institut für Mechanische Verfahrenstechnik und Mechanik, Universität Karlsruhe (TH)
Dept. of Chemical Engineering, University of California at Los Angeles (UCLA), Los Angeles CA

Introduction

- Continuous regeneration of soot traps at low temperatures desirable
- Soot trap design requires knowledge on reaction mechanism
- NO seems to play an important role in catalytic soot oxidation

CO_2

NO

NO

NO_2

$O^* \, O_2$

porous support
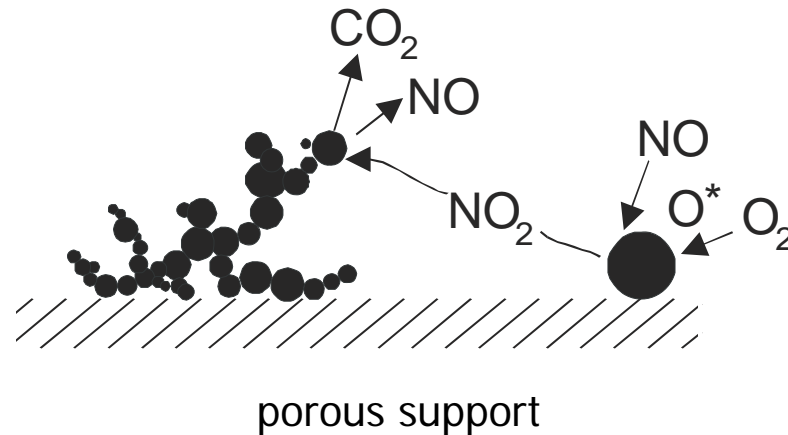
Our contribution:

Investigation of effects of
- particle size of Pt-catalysts
- interparticle distance between soot and catalyst
  on the rate of soot oxidation in a simulated diesel exhaust gas

Using
- Aerosol methods for the generation of tailored catalyst particles
- Microscale experiments

Experimental system

soot particle

Pt- catalyst

TEM grid
(SiO2)
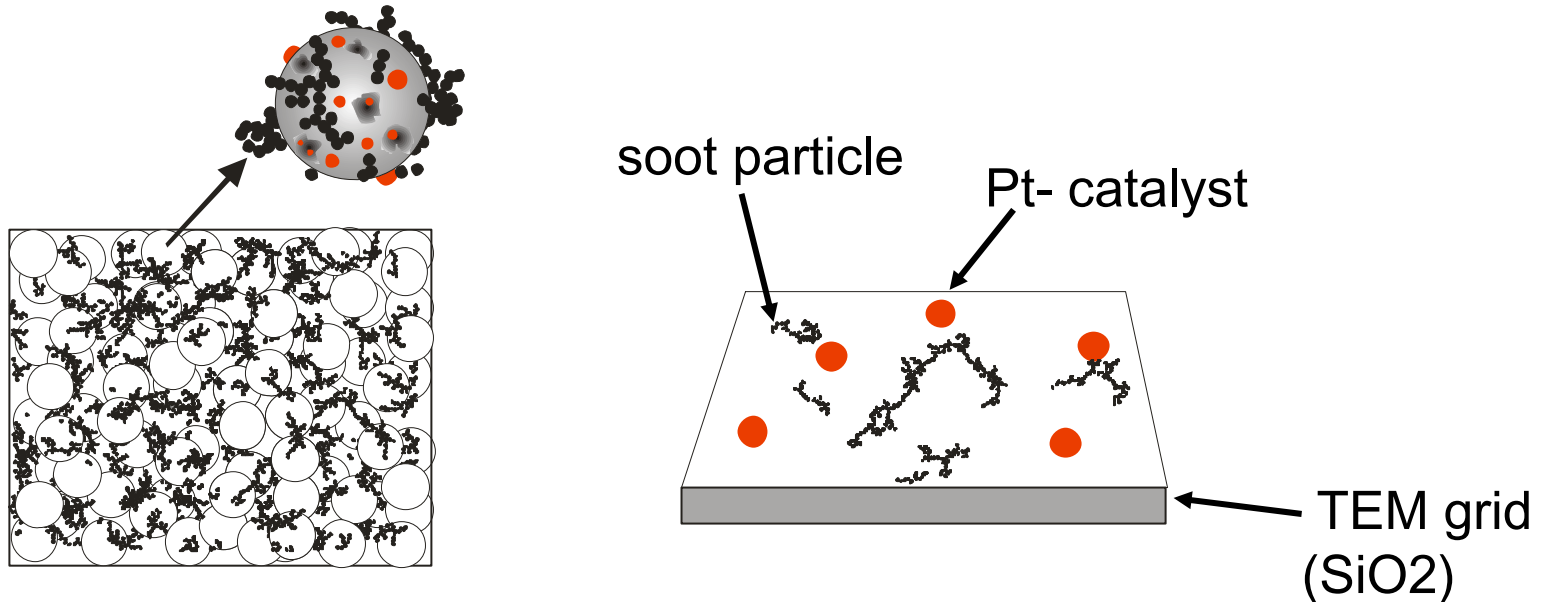
macroscopic experiments (thermogravimetry, DTA):

Contact between soot and catalyst ill defined; heat and mass transfer limited.
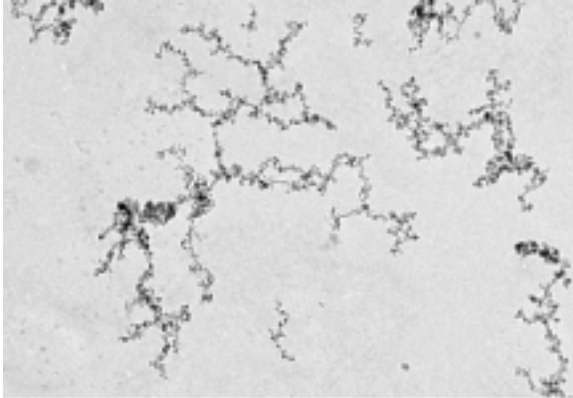
microscale experiments:

Local information on interparticle distance and particle size; good simulation of the practical system
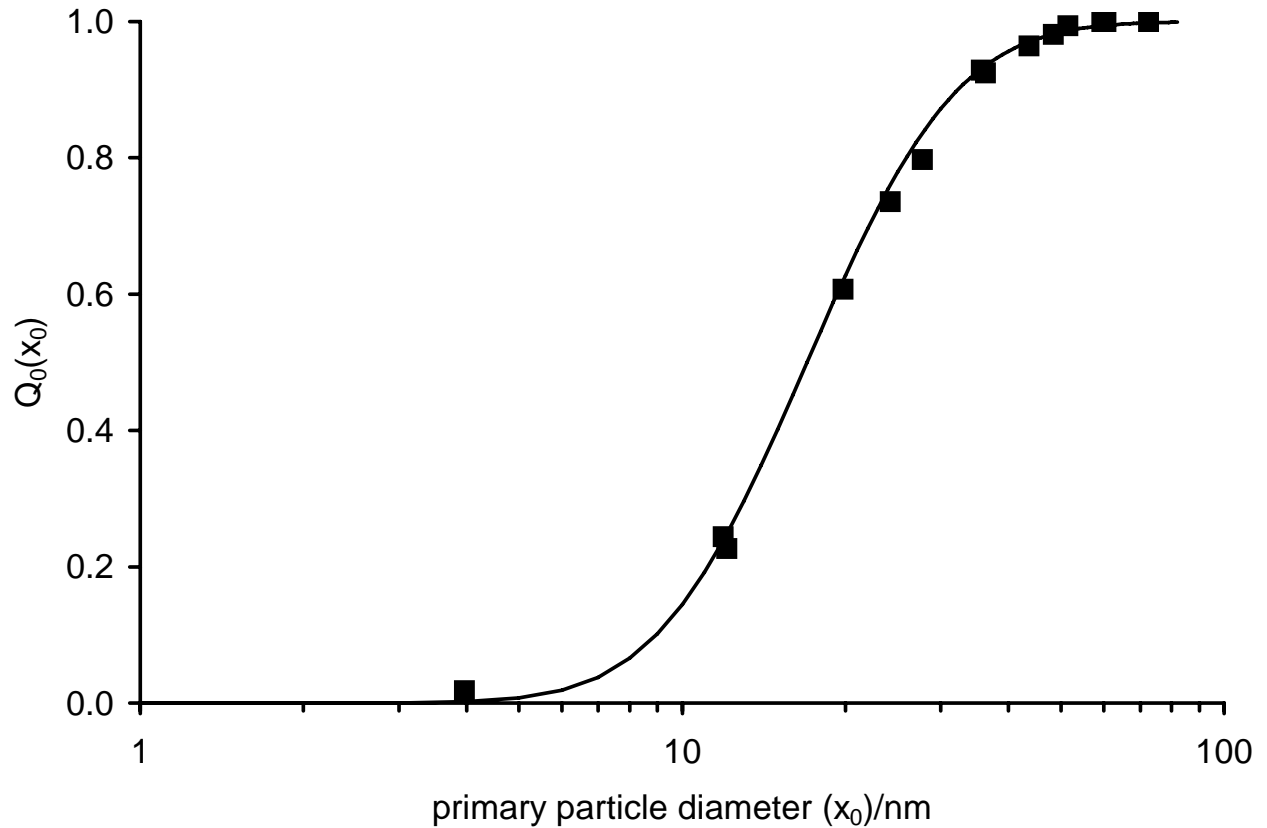
catalyst generation
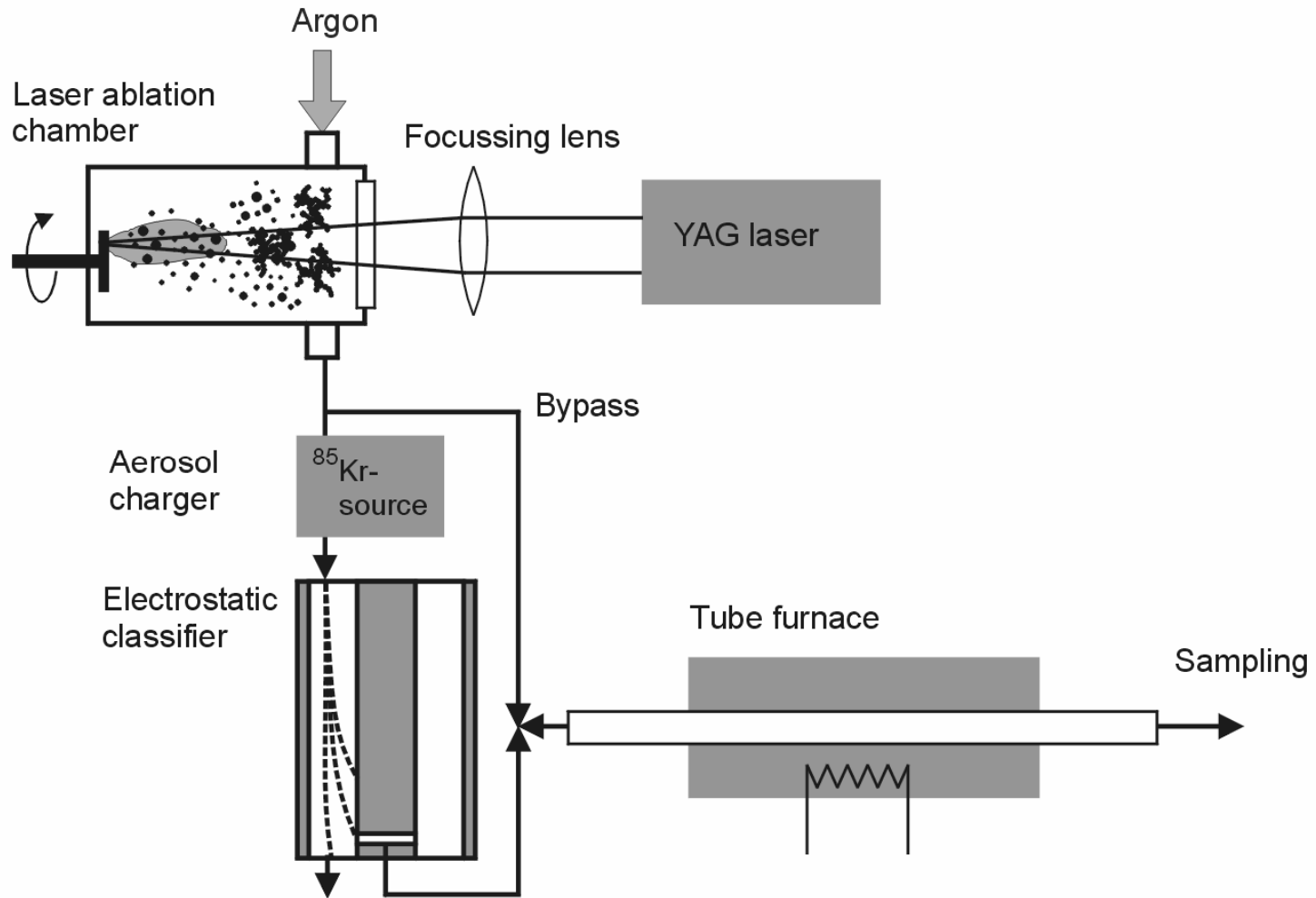
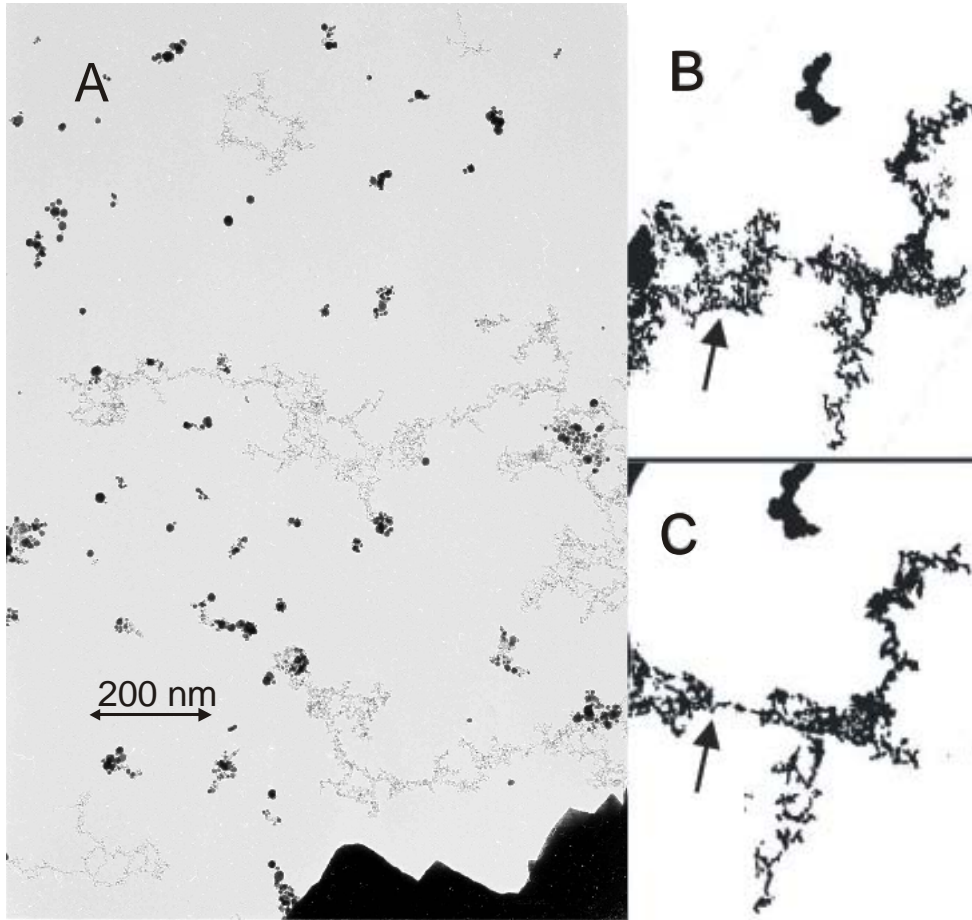# Pt-catalysts
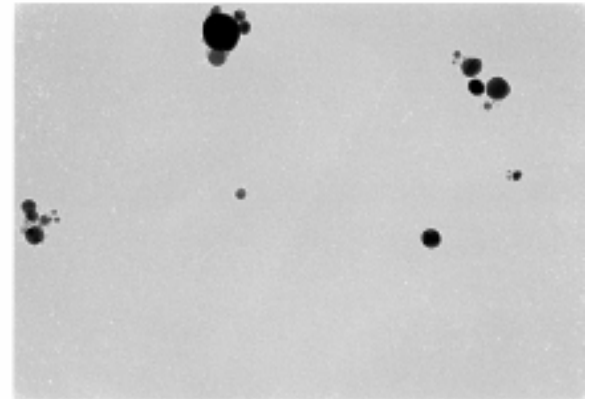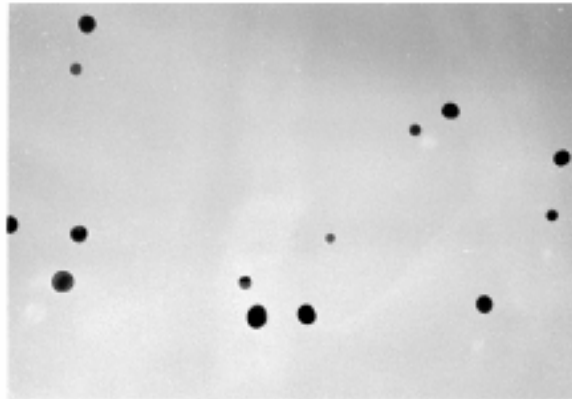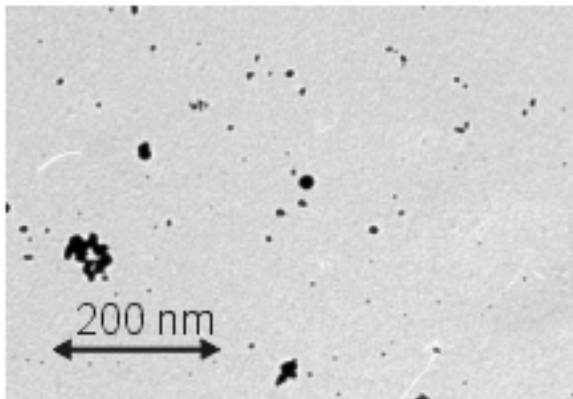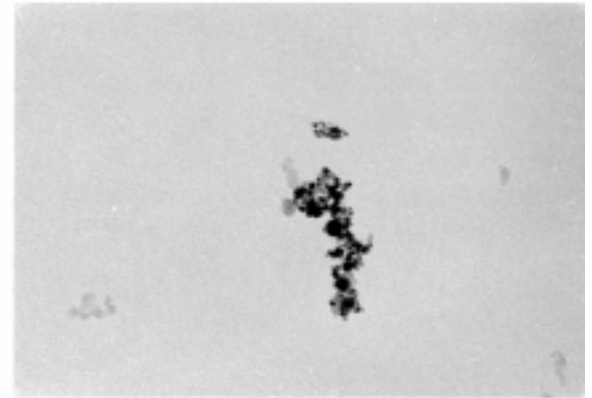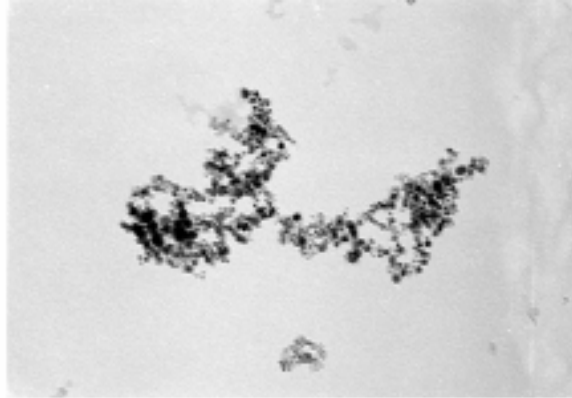
Primary particles: 7-31 nm

Model soot

Generated by laser
ablation from a
graphite target

Evaluation

- Projected area of C-agglomerates determined from TEM micrographs
- Comparison with projected area of primary particle yields number of primaries N
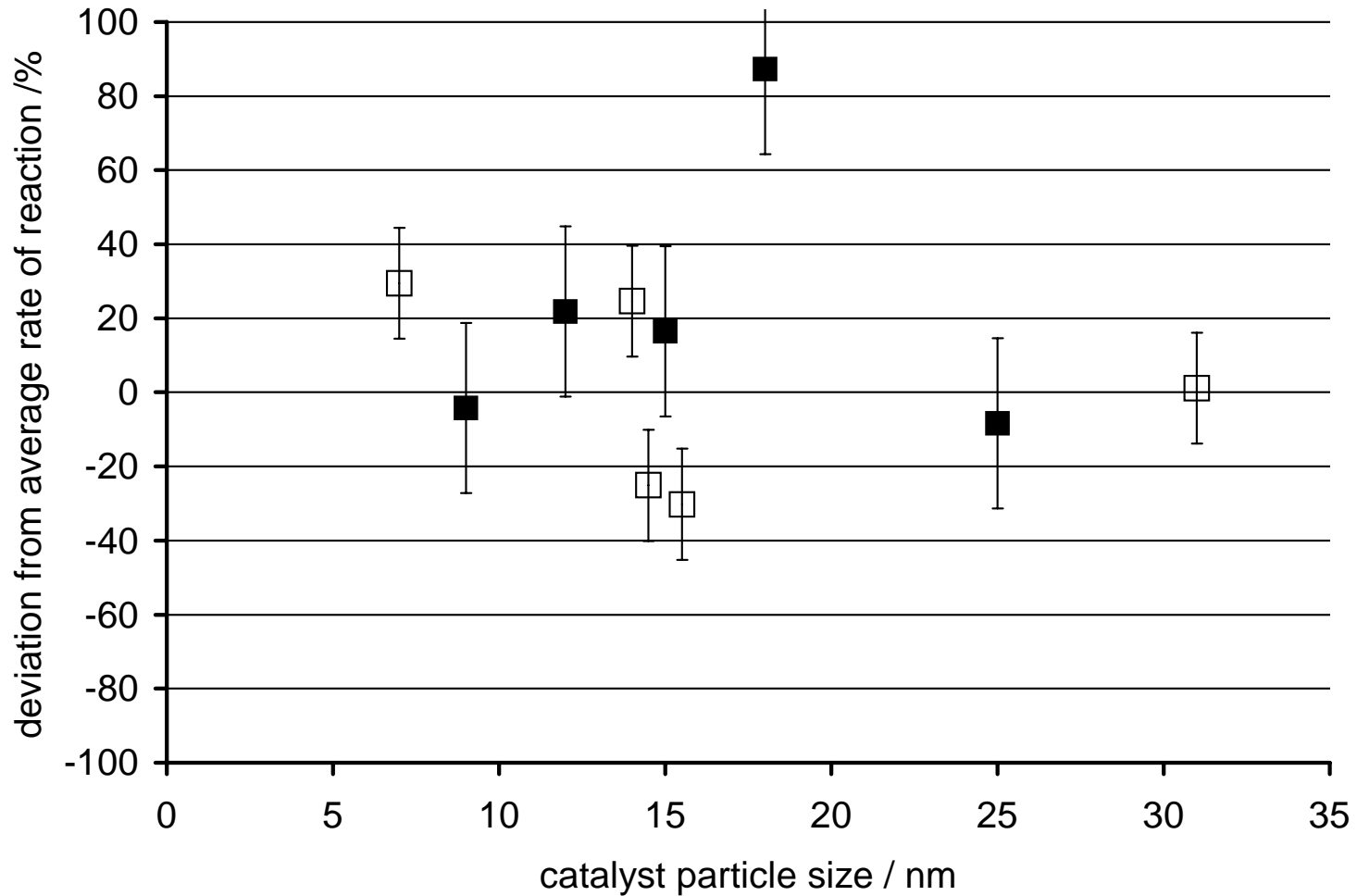- N and $x_{m,3}$ yields carbon volume

Reaction conditions:
  T: 300 °C
  c_{NO}:1000 ppm
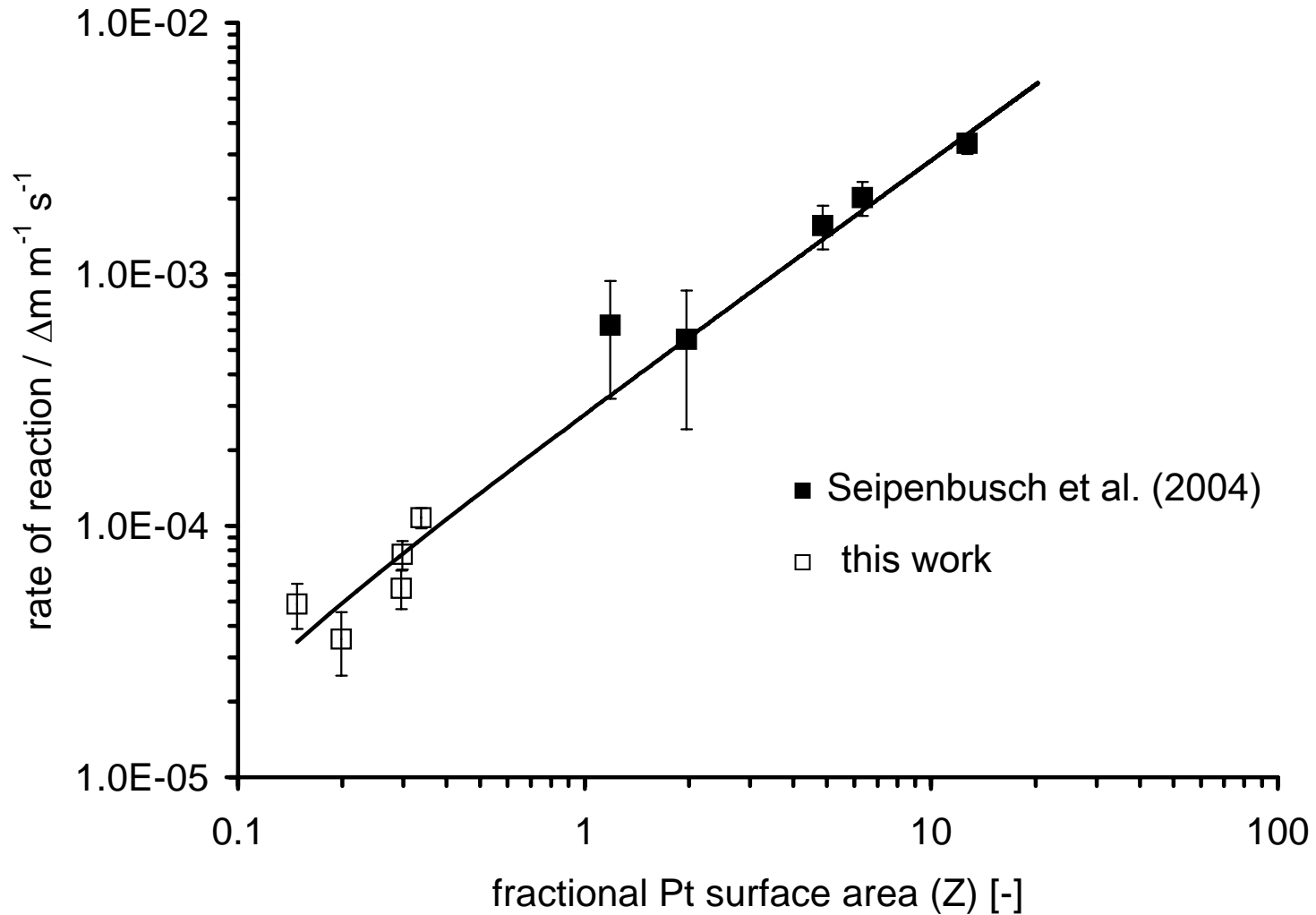 c_{O2} 10%

Effect of Pt particle size on reaction rate

Rate of reaction vs. Pt surface area

Plot of rate of reaction / Δm m^{-1} s^{-1} versus fractional Pt surface area (Z) [-]. Legend: ■ Seipenbusch et al. (2004); □ this work.

Influence of proximity C-Pt
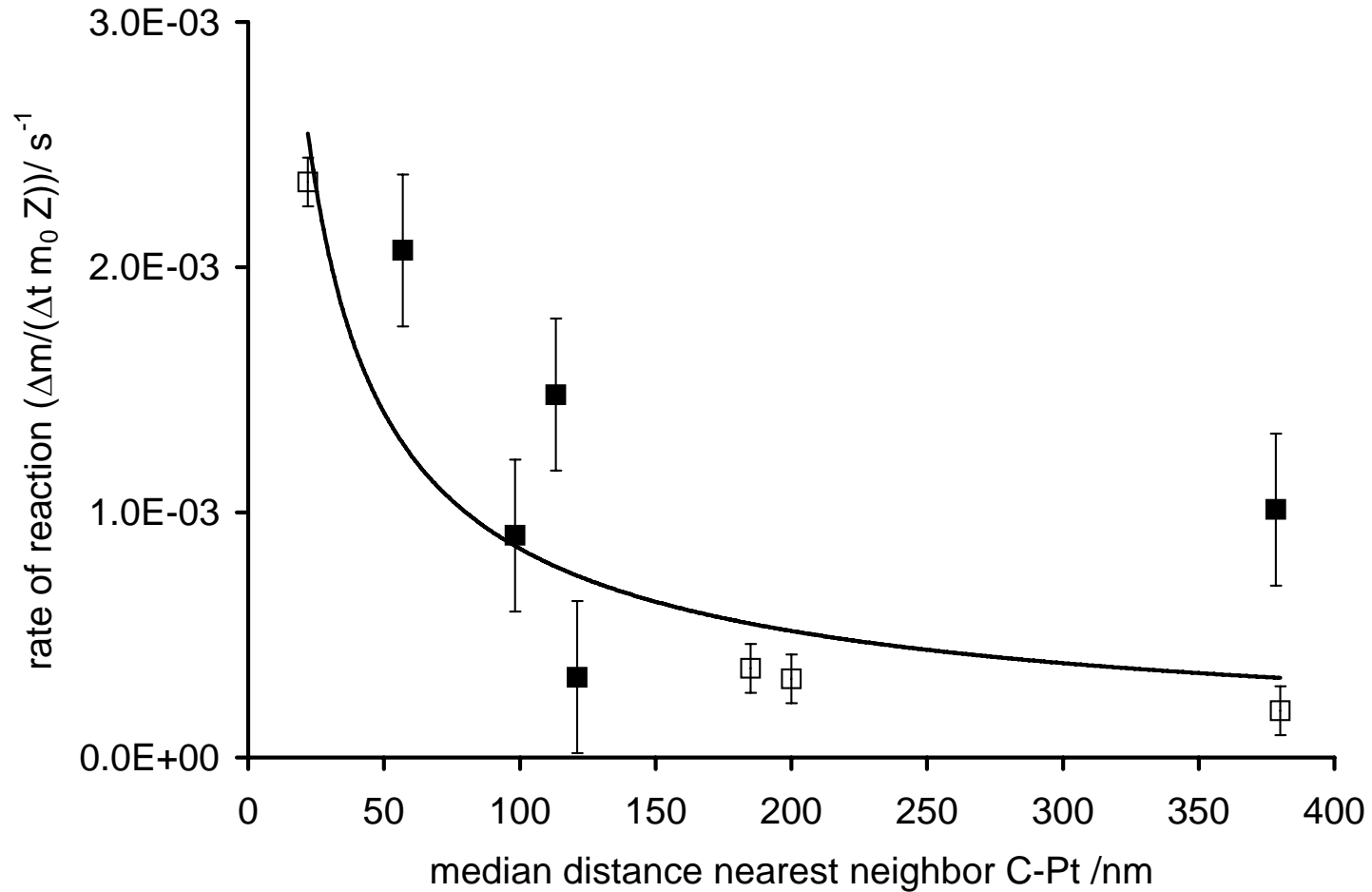
Summary and Conclusions

- No apparent relationship between Pt particle size and reaction rate as pure size effect

- Linear dependance reaction rate-Pt surface area over a wide range

- Inverse relationship reaction rate median nearest neighbor distance

  ➡ soot oxidation seems to be first order with respect to NO_2