



## Effect of NO<sub>2</sub> and water on the catalytic oxidation of soot



Jakob M. Christensen<sup>a,\*</sup>, Jan-Dierk Grunwaldt<sup>a,b</sup>, Anker D. Jensen<sup>a</sup>

<sup>a</sup> Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søtofts Plads B229, 2800 Kgs. Lyngby, Denmark

<sup>b</sup> Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, Engesserstrasse 20, 76131 Karlsruhe, Germany

### ARTICLE INFO

#### Article history:

Received 24 September 2016

Received in revised form 4 December 2016

Accepted 7 December 2016

Available online 8 December 2016

#### Keywords:

Soot oxidation

Nitrogen dioxide

Mars van Krevelen mechanism

Volcano curve

Spillover

### ABSTRACT

The influence of adding NO<sub>2</sub> to 10 vol% O<sub>2</sub>/N<sub>2</sub> on non-catalytic soot oxidation and soot oxidation in intimate or loose contact with a catalyst has been investigated. In non-catalytic soot oxidation the oxidation rate is increased significantly at lower temperatures by NO<sub>2</sub>. For soot oxidation in tight contact with a Co<sub>3</sub>O<sub>4</sub> catalyst a more reactive NO<sub>2</sub>-containing atmosphere did not change the oxidation profile significantly during temperature programmed oxidation. This is consistent with the expected Mars van Krevelen mechanism, where the rate limiting step is reaction between carbon and lattice oxygen from the oxide, and where the reaction thus has reached the zero order kinetics regime in the gaseous reactant. In loose contact with a catalyst the presence of NO<sub>2</sub> causes a pronounced enhancement of the oxidation rate. The rate constants for loose contact soot oxidation in the presence of NO<sub>2</sub> exhibited a volcano-curve dependence on the heat of oxygen chemisorption, and among the tested pure metals and oxides Cr<sub>2</sub>O<sub>3</sub> was the most active catalyst. Further improvements were achieved with a Fe<sub>3</sub>Cr<sub>6</sub>O<sub>x</sub> binary oxide catalyst.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

Soot particles in the exhaust from diesel vehicles adversely affect human health [1–3], and are therefore typically removed from the exhaust gas by filtration through a ceramic filter [4–6]. As the filter becomes blocked by the soot particles, periodic regeneration is necessary. For this purpose the filter temperature is increased, and the soot is oxidized. The growing back pressure due to the soot deposits and the temperature increase required for filter regeneration are associated with increased fuel consumption [7], and it is desirable to develop improved soot oxidation catalysts that can lower the regeneration temperature [4]. Being a gas/solid/solid interaction, where the contact between soot and catalyst is very important, the catalytic effect depends strongly on the intimacy of mixing between soot and catalyst [8,9]. In laboratory tests, where soot and catalyst are crushed together (so-called tight contact), the oxidation occurs at a significantly lower temperature (typically 100–200 °C), than if soot and catalyst are mixed together gently (so-called loose contact) [8,9]. In tight contact an extensive interface between the primary particles of soot and catalyst is established, but in loose contact the interface is limited to isolated contact points between larger clusters of the primary particles [10]. A number of filtration experiments have shown indications of

reactivity corresponding to both contact types [11–17]. It therefore seems likely that both types of contact would be relevant for real filter applications.

To enable the development of improved soot oxidation catalysts the factors that determine the catalytic activity need to be identified. As expected the surface area of the employed catalyst is important [18,19]. The strength of the oxygen-catalyst bond, as measured by the heat of oxygen chemisorption, is also very important for the catalytic activity [20]. For both tight and loose contact tests with O<sub>2</sub> as the oxidant the rate constants for various metal or metal oxide catalysts resulted in a volcano curve if plotted as function of the heat of oxygen chemisorption for the catalytic materials [20]. In tight contact materials such as Co<sub>3</sub>O<sub>4</sub> and CeO<sub>2</sub> that bind oxygen more weakly were found to be nearest to the optimal bond strength, while the more strongly binding Cr<sub>2</sub>O<sub>3</sub> was nearest to the activity optimum in loose contact [20]. The shift in the optimal material may reflect the existence of multiple reaction pathways that contribute with different relative weight in the two cases. In tight contact tests TEM studies [21,22], isotopic labeling studies [23–28] and XPS studies [29] have indicated that the oxidation primarily occurs at the soot/catalyst interface by a Mars van Krevelen [30] mechanism, namely an initial oxidation by catalyst lattice oxygen followed by re-oxidation of the catalyst. The rate limiting step is most likely the reaction of lattice oxygen with carbon, since the reaction rate depends on both the oxygen bond strength of the catalyst [20] and the inherent reactivity of the soot [19]. In loose contact tests the activation of oxygen occurs on the oxide [28,31–34], and

\* Corresponding author.

E-mail address: [jmc@kt.dtu.dk](mailto:jmc@kt.dtu.dk) (J.M. Christensen).

most likely the activated oxygen then diffuses to the soot [35–37], and reacts at the most reactive defect sites [38,39]. A catalytic effect is also present in experiments where soot and catalyst are separated by an inert (and insulating) material that the activated oxygen must pass to reach the soot [32,36], and it therefore seems likely that the oxygen activation is by dissociative chemisorption into atomic oxygen that would remain reactive [40] also when removed from the catalyst surface.

The absolute rate of soot oxidation will also depend on the gas atmosphere [41–43]. The example of greatest practical importance is that many filter regeneration strategies for diesel vehicles involve acceleration of the soot oxidation by catalytically oxidizing NO in the exhaust gas to NO<sub>2</sub> [44–46], which is a more reactive oxidant than O<sub>2</sub> [46–50]. There are known examples, where the volcano curve for a catalytic reaction, and thus the optimal choice of catalyst, is shifted depending on the gas atmosphere [51,52]. It is therefore relevant to evaluate, how the components in the gas atmosphere, particularly NO<sub>2</sub>, influence the catalytic reaction and optimal choice of catalyst, also as a function of the contact between soot and catalyst. This is the topic of the present paper. Additionally, this work provides global kinetic parameters for the occurring oxidation reactions, which may be of use for CFD-based models of soot combustion dynamics in catalytic diesel particulate filters [53,54].

## 2. Experimental

### 2.1. Catalysts used for screening experiments

The catalysts used in the screening studies were the bulk oxides or metals also used in our previous study, where the identities of the catalysts were confirmed by XRD [20]. In the cases of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Pd and Pt black commercially acquired samples from Sigma-Aldrich were used. In the cases of CeO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, MnO<sub>x</sub>, ZnO and Cr<sub>2</sub>O<sub>3</sub> the oxide samples were prepared by flame spray pyrolysis according to the method described elsewhere [19,20].

### 2.2. SiO<sub>2</sub> supported FeCr<sub>2</sub>O<sub>x</sub> binary oxide catalyst

An SiO<sub>2</sub> supported FeCr<sub>2</sub>O<sub>x</sub> catalysts also employed in our previous study [20] was used. SiO<sub>2</sub> extrudates (Saint-Gobain, 250 m<sup>2</sup>/g) were impregnated with an aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Sigma Aldrich) to produce FeCr<sub>2</sub>O<sub>x</sub>/SiO<sub>2</sub> with a total metal loading of 14.8 wt%. The impregnated sample was aged for 2 h and then dried at 110 °C overnight. The dried catalyst precursor was then calcined in stagnant air for 2 h at 500 °C (ramp: 20 °C/min). Finally the calcined catalyst was crushed to <300 μm and used in the powdered form. The XRD pattern of the catalyst contains the reflections from  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> shifted slightly downwards towards the reflections from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> suggesting the formation of a mixed oxide [20].

### 2.3. Catalytic soot oxidation

The catalytic activity in soot oxidation was measured using a flow reactor setup described elsewhere [20]. For the activity tests soot (~2 mg, NIST SRM 2975) and catalyst in a ratio of 1:5 (wt:wt) were stirred together with a spatula (loose contact) or crushed together for 6 min in an agate mortar (tight contact). The silica supported Fe-Cr binary oxide catalyst was tested at a higher soot:catalyst ratio of 1:10 (wt:wt) due to the lower fraction (15 wt%) of active material in this sample. The soot/catalyst mixture was transferred to a 7 cm long, 1 cm wide alumina sample holder, which was placed in the center of a quartz tube (length: 65 cm, inner diameter: 24 mm) within a horizontal, tubular furnace. The sample was then subjected to a 1 NL/min flow of 10.2 vol% O<sub>2</sub> in N<sub>2</sub> (in some cases the feed also contained 934 ppmv NO<sub>2</sub> or 887 ppmv

NO<sub>2</sub> and 5 vol% H<sub>2</sub>O). The feed gases (N<sub>2</sub>, O<sub>2</sub> and 1040 ppmv NO<sub>2</sub> in N<sub>2</sub>—all from AGA A/S) were dosed by means of Bronkhorst EL-FLOW mass flow controllers. Distilled water was fed using a Knauer K-120 HPLC pump. When the sample had been installed in the oven, and once any remnants of air had been purged from the reactor (when the CO<sub>2</sub> signal from ambient air had fallen below the detection limit) the reactor was heated at a rate of 11 °C/min to a final temperature of 750 °C. The temperature was monitored by a type K thermoelement at the external surface of the quartz tube wall. The concentrations of CO and CO<sub>2</sub> in the reactor effluent were monitored continuously using an ABB AO2020 IR gas analyzer calibrated using a certified CO/CO<sub>2</sub>/N<sub>2</sub> gas mixture from AGA A/S. When water was fed, the reactor effluent was passed through an ice cooled U-tube condenser to avoid that water interfered with the CO/CO<sub>2</sub> analysis. During the experiments with NO<sub>2</sub> the levels of CO and CO<sub>2</sub> in the effluent stream were in the 0–200 ppmv range. The conversion of gaseous reactants due to the soot oxidation was thus relatively limited, and the dependence on the oxidant concentration was omitted in the kinetic analyses.

The soot used in the present experiments was a reference material from NIST: “SRM 2975 Diesel Particulate Matter” (from an Industrial Forklift). Various characterizations of this carbonaceous material can be found in the literature [19,55–57].

### 2.4. Kinetic analysis

The results have been interpreted in terms of a simple, global kinetic model (assuming differential conditions in the gas phase), where catalytic and non-catalytic oxidation by O<sub>2</sub> and NO<sub>2</sub> are assumed to occur by 4 parallel reactions:

$$\frac{dX}{dt} = k_{NO_2,cat}(1-X)^{2/3} + k_{O_2,cat}(1-X)^{2/3} + k_{NO_2,non-cat} \cdot (1-X)^{2/3} + k_{O_2,non-cat} \cdot (1-X)^{2/3}$$

Here  $X$  is the degree of carbon conversion, and  $k$  is the rate constant for either catalytic or non-catalytic oxidation by either O<sub>2</sub> or NO<sub>2</sub>. The degree of conversion is obtained from numerical integration of the CO and CO<sub>2</sub> signals. The kinetic parameters for soot oxidation by O<sub>2</sub> were taken from our previous study of oxidation in the absence of NO<sub>2</sub> [20]. The kinetic parameters for non-catalytic oxidation by NO<sub>2</sub> were determined in the absence of a catalyst, and the kinetic parameters for catalytic oxidation by NO<sub>2</sub> are then fitted to the results from the present catalytic experiments. The obtained kinetic parameters are listed in table S2 in the supplementary information. The assumption of oxidation by O<sub>2</sub> and NO<sub>2</sub> as parallel reactions is supported by the results of Arthur et al. [49]. Across all the tested samples (both non-catalytic oxidation as well as loose and tight contact catalytic oxidation) the best fit for the simple kinetic model was achieved with a carbon reaction order of 2/3. This is consistent with the soot particles behaving as uniformly shrinking spheres [58]. However, as discussed elsewhere [59], other types of behavior may lead to similar reaction orders. An evaluation of the present results in terms of the temperature of maximal oxidation rate (the optimum between the increase in reaction rate with temperature and the decline in reaction rate with increasing reactant consumption), which is another common measure of activity in soot oxidation, generally yields the same conclusions, and such an analysis is provided in the supplementary information (Fig. S1).

Download English Version:

<https://daneshyari.com/en/article/6454303>

Download Persian Version:

<https://daneshyari.com/article/6454303>

[Daneshyari.com](https://daneshyari.com)