



# Modelling of the kinetics of the catalytic soot oxidation on $\text{Fe}_2\text{O}_3$

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## ABSTRACT

This paper addresses the kinetic modelling of the soot oxidation on a  $\text{Fe}_2\text{O}_3$  model catalyst. The kinetics was evaluated by temperature programmed oxidation using a packed bed of tight contact mixtures of  $\text{Fe}_2\text{O}_3$  and soot. The reaction rate was expressed by a global-kinetic approach taken from a previous paper. Some kinetic parameters were determined by a fit to experimental TPO data using a stationary 1-D CSTR model with coupled mass and heat balance. The fitting led to an apparent activation energy of 73 kJ/mol, while the pre-exponential factor was calculated to be  $1.6 \times 10^3 \text{ m}^3/(\text{mol s})$ . The kinetic model was validated by simulations and was then implemented into a transient 2-D model of the fixed-bed reactor. This model implied the conservation of mass, heat and momentum and was checked by temperature measurements conducted with an IR camera. Finally, the 2-D model was validated by simulating some TPO investigations. The simulations provide local concentrations of  $\text{CO}_2$ ,  $\text{O}_2$  and soot as well as local temperature and gas velocity. Particularly, these results suggest the absence of any drastic gradients of concentration and temperature in the packed bed due to the convection of the gas stream.

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## 1. Introduction

Diesel particulate filters (DPF) represent a common technology for the separation of soot from diesel exhaust. However, these filter systems need to be regenerated, as the trapped soot can cause backpressure effects potentially decreasing the engine efficiency [1]. Thus, several techniques were developed for the DPF regeneration, which imply the oxidation of the carbonaceous soot fraction, whereas ash entities remain in the filter. These procedures recently summarised in this journal [2] are (i) the Continuously Regenerating Trap (CRT) [3], which uses  $\text{NO}_2$  for the initiation of the soot/ $\text{O}_2$  reaction, (ii) organometallic Fuel Borne Catalysts decreasing the soot output of the engine and enhancing the oxidation of the filtered soot [4], and (iii) the post-injection of fuel causing rise in temperature [4,5]. Furthermore, the catalytic soot oxidation by  $\text{O}_2$  is considered to be a promising alternative including a catalytic coating on the DPF (CDPF). A multitude of oxide catalysts was reported in the literature to enhance the soot/ $\text{O}_2$  reaction, e.g.  $\text{V}_2\text{O}_5$  [6],  $\text{CeO}_2$  [7,8] and  $\text{Fe}_2\text{O}_3$  [9]. But, up to now the CDPF technique reveals only limited benefit under real exhaust conditions due to insufficient contact of the catalytic coating and the soot deposited on it [10].

Mechanistic investigations showed that the role of the catalyst is to transfer oxygen from its surface to the soot [11]. Three basic oxygen transfer mechanisms are known for oxide catalysts [11–13]. (1) In the surface redox mechanism, e.g. reported for  $\text{Co}_3\text{O}_4$ , surface

oxygen of the catalyst is transferred at the interface to the soot, whereas the resulting vacancies of the catalytic surface are filled by gas-phase oxygen. (2) The spill-over mechanism occurring on  $\text{CeO}_2$  and  $\text{Cr}_2\text{O}_3$  for instance implies dissociative adsorption of oxygen on the catalyst surface followed by transfer of atomic oxygen to the soot [12]. In this route, a contact of both solids is not explicitly required. (3) The redox mechanism reveals transfer of bulk oxygen from the catalyst to the contact points of both solids under local reduction of the catalyst; a prominent example is  $\text{V}_2\text{O}_5$  [12]. The catalyst is then re-oxidised by gas-phase oxygen. In respect of  $\text{Fe}_2\text{O}_3$ , both surface [12,14,15] as well as bulk redox mechanism [2] was postulated in the literature. Additionally, another mechanism described for  $\text{K/CeO}_2$  involves the formation of super oxides [16].

Moreover, catalysts were also classified into mobile and non-mobile systems. Mobile catalysts are alkaline, earth alkaline and several transition metals with low melting points [11,17,18]. These catalysts are capable of migrating onto the soot surface thus continuously forming new contact points. Contrary, non-mobile catalysts are temperature resistant oxides such as  $\text{CeO}_2$  [7] and  $\text{Fe}_2\text{O}_3$  [7,9,18], which essentially require contact to the soot. The effect of the type of contact on the soot oxidation was demonstrated by several groups indicating that intimate mixing of both solids enhances the soot oxidation [19,20]. Also, it was shown that soot oxidation can be strongly affected by the amount and heat capacity of the catalyst acting as a temperature buffer [2,21]. Furthermore, a global reaction mechanism of soot oxidation on  $\text{Fe}_2\text{O}_3$  was reported implying the transfer of surface and crystal oxygen to the soot, the regeneration of oxygen vacancies and exchange of surface oxygen by  $\text{CO}_2$  and  $\text{O}_2$  adsorption [2,9,13].

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For the use of iron oxide catalysts in the CDPF technique the present paper aims to contribute to a fundamental understanding of the oxidation of soot employing an  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> model catalyst. We report on kinetic investigations as well as a global-kinetic model, which we stepwise implemented into a stationary 1-D model and then a transient 2-D model.

## 2. Experimental

### 2.1. Preparation and characterisation of the Fe<sub>2</sub>O<sub>3</sub> catalyst and soot

The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> model catalyst was synthesised by polyvinyl alcohol (PVA) method as described in detail elsewhere [22]. Briefly, the remaining residual of the evaporated solution of aqueous Fe(NO<sub>3</sub>)<sub>3</sub> and PVA was calcined in static air atmosphere at 600 °C for 5 h. The crystalline structure was analysed by powder X-ray diffraction (PXRD) on a D8 Advance (Bruker) using Ni filtered Cu K $\alpha$  radiation. The BET surface area was examined by multi-point Sorptomatic 1990 (Porotec) taking N<sub>2</sub> as adsorbate. Before recording the isotherm at –196 °C, the sample was pre-treated at 300 °C for 2 h in vacuum (10<sup>–4</sup> mbar). From the adsorption data taken at  $p/p_0$  ratios between 0.05 and 0.30 the BET surface area was derived. The BET surface area of the catalyst was determined to be 15 m<sup>2</sup>/g.

The soot was prepared by burning a C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub> mixture in a diffusion flame and was collected by a particulate filter [23]. The most important physical–chemical properties of the soot are as follows: BET surface area: 90 m<sup>2</sup>/g, amount of adsorbed species: 4 wt.%, chemical composition (adsorbed species neglected): 97.5 wt.% C, 1.5 wt.% O, 0.6 wt.% H, 0.2 wt.% N, soot is ashless, mean diameter of primary particles: 45 nm.

### 2.2. Kinetic studies

The kinetics of the soot oxidation on the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> model catalyst was investigated by using the temperature programmed oxidation (TPO). In TPO, the temperature was linearly increased from room temperature to 500 °C at a rate of 3.3 K/min. The total gas flow was kept at 500 ml/min (STP) and consisted of 10 vol.% O<sub>2</sub> and 90 vol.% N<sub>2</sub> both supplied by independent flow controllers (MKS Instruments). Effluent CO and CO<sub>2</sub> were analysed by a non-dispersive infrared spectrometer (Binos 1.2, Leybold-Heraeus). The experiments were performed with a tight contact catalyst/soot mixture implying 10 mmol catalyst and 5 mmol soot ( $m_{total} = 1.66$  g). Tight contact mixture was established by ball milling the catalyst/soot blend for 15 min employing a Pulverisette 0 (Fritsch) with a hardened steel ball ( $m = 940$  g); ball milling results in a contact mode being close to soot deposited on a catalytic DPF under full load conditions of the engine. After mixing, the respective mixture was pressed for 2 min at 4 MPa, granulated and sieved to a mesh of 125–250  $\mu$ m to avoid discharge in the catalytic tests. Former investigations demonstrated that pressing and granulating do not affect the activity of the mixture, whereas the ball milling was found to be the crucial step of preparation [22]. Finally, the catalyst/soot mixture was placed in the quartz glass tube reactor (i.d. 10 mm) as packed bed fixed by quartz wool. The gas temperature was monitored by two K-type thermocouples located directly in front of and behind the bed.

The development of the local temperature of the tight contact catalyst/soot mixture was investigated by using an IR camera. A TPO was performed in a special stainless steel reactor (i.d. 10 mm) implying a sapphire window located above the packed bed. The temperature of the surface of the catalyst/soot bed was recorded by a Pyroview 380M camera (DIAS). The heating rate was 8.6 K/min.

## 3. Results and discussion

### 3.1. Modelling of the chemical kinetics

#### 3.1.1. Development of a 1-D reactor model

For the development of a 1-D model a suitable reactor model was evaluated by determining the Bodenstein ( $Bo$ ) number of the packed bed. We used an approach from Aris, which states the additivity of means and variances of the mean residence time distribution [24]. The mean residence time  $\bar{t}$  and the variance  $\sigma^2$  of the tube reactor ( $\bar{t} = 37.8$  s,  $\sigma^2 = 68.2$  s<sup>2</sup>), which includes the packed bed, and the empty tube reactor ( $\bar{t} = 36.3$  s with  $\sigma^2 = 40.9$  s<sup>2</sup>), shortened by the length of the packed bed, were determined by step experiments [25]. This facilitates the identification of the  $Bo$  number of the packed bed Eq. (1) resulting in  $Bo = 0.4$  characterising a CSTR.

$$\frac{\sigma_2^2 - \sigma_1^2}{(\bar{t}_2 - \bar{t}_1)^2} = \frac{\Delta\sigma^2}{(\Delta\bar{t})^2} = \frac{1}{2 \cdot Bo} \quad (1)$$

Additionally, the  $Bo$  number of the packed bed was also estimated from the axial Peclet number ( $Pe_{a,p}$ ) according to the equation of Edwards and Richardson, i.e.  $1/Pe_{a,p} = 0.3/(Sc Re_p) + 0.5/(1 + 3.8/(Re_p Sc))$ ;  $Re_p$  is the particle Reynolds number and  $Sc$  is the Schmidt number [26]. With  $Bo = Pe_{a,p} L/d_p$  ( $L$ , length of packed bed,  $d_p$  particle diameter)  $Bo$  is estimated to be 2 being close to the experimental result. Furthermore, packed beds with  $Bo$  numbers below 1 were also reported in the literature for similar conditions [27]. Nevertheless, it should be mentioned that the experimental  $Bo$  number is based on several simplifications. The retention time was measured at room temperature and possible changes in the packed bed due to conversion of soot upon TPO are not considered.

#### 3.1.2. Coupling of kinetics and CSTR model

The rate of the CO<sub>2</sub> formation (Eq. (2)) is described by a global-kinetic expression depending on the concentration of gaseous O<sub>2</sub> ( $c(O_2)$ ) and the molar amount of active carbon sites ( $n(C^*)$ ) [14]. The rate constant  $k_{CO_2}$  is expressed by an Arrhenius-based approach.  $n(C^*)$  is derived from a random pore model [9] which implies the surface concentration of active sites ( $\lambda$ ), soot conversion ( $X$ ), initial BET surface area ( $S_0$ ), soot mass at conversion  $X$  ( $m(X)$ ) and semi-empiric structural factor of soot ( $f$ ) addressing the pore structure resulting in Eq. (3) [11].

$$r(CO_2) = \frac{dn(CO_2)}{dt} = k_{CO_2} \cdot n(C^*) \cdot c(O_2)^n \quad (2)$$

$$r(CO_2) = A \cdot \exp\left(\frac{-E}{RT}\right) \cdot m_0 \cdot (1 - X) \cdot S_0 \cdot \sqrt{1 + f \cdot X} \cdot c(O_2)^n \quad (3)$$

Moreover, the calculation of the Mears [28] and Weisz-Prater criteria [29] excludes mass transfer limitation by film and pore diffusion. However, it is known that the exothermic reaction and heat capacity of the packed bed [2] strongly affect the chemical kinetics of soot oxidation. Hence, Eq. (3) is coupled with the mass (Eq. (4));  $\tau$ : hydrodynamic retention time,  $V_{bed}$ : bed volume) and energy balance (Eq. (5)) of the stationary CSTR;  $m$  is the reaction mass,  $c_{p,bed}$  the heat capacity of the bed volume,  $c_{p,gas}$  the heat capacity of the gas,  $\Delta H$  the reaction heat,  $k$  the heat transfer coefficient and  $A$  is the heat transfer area.

$$\frac{dc(CO_2)}{dt} = \frac{1}{\tau} (c(CO_2)_{in} - c(CO_2)_{out}) + \frac{r(CO_2)}{V_{bed}} \quad (4)$$

$$m \cdot c_{p,bed} \cdot \frac{dT}{dt} = F \cdot c_{p,gas} \cdot (T_{furnace} - T) - r(CO_2) \cdot \Delta H - k \cdot A \cdot (T - T_{furnace}) \quad (5)$$

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