



Oxidation of soot on manganese oxide catalysts

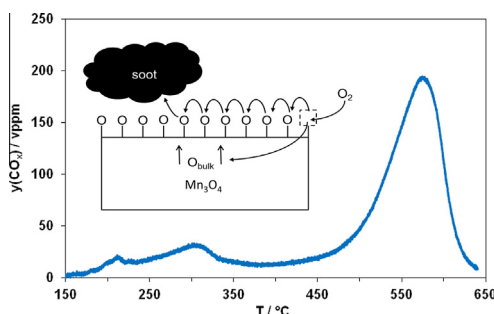
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HIGHLIGHTS

- Soot oxidation on manganese oxides is driven by surface oxygen vacancies and particle size of the catalysts.
- Bulk oxygen strongly contributes to oxygen transport from catalyst to soot.
- Mn_3O_4 prepared by flame spray pyrolysis is one of the most effective soot oxidation catalysts.

GRAPHICAL ABSTRACT



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ABSTRACT

The present paper deals with the catalytic oxidation of soot by O_2 on bare manganese oxides. The catalysts comprised MnO_2 , Mn_2O_3 and Mn_3O_4 as well as nano-sized Mn_3O_4 originated from flame spray pyrolysis (FSP- Mn_3O_4). The activity of the samples was evaluated by temperature programmed oxidation (TPO) using tight and loose contact catalyst/soot mixtures.

The catalysts were characterised by powder X-ray diffraction, N_2 physisorption, scanning electron microscopy, temperature programmed reduction by H_2 and temperature programmed desorption of NH_3 . The correlation of physical–chemical characteristics with soot oxidation kinetics showed that the number of surface oxygen vacancies and particle size determine the catalytic performance by affecting the supply of oxygen. Isotopic TPO studies of FSP- Mn_3O_4 /soot suggested that oxygen was transferred from the surface and bulk of the catalyst to the soot by physical contact points. A strong contribution of bulk oxygen (ca. 60%) occurred for tight as well as loose contact. The role of gas-phase O_2 was found to refill the oxygen vacancies of the catalyst.

Furthermore, FSP- Mn_3O_4 showed the best performance among the samples tested. The catalyst revealed high efficiency for tight contact yielding peak CO_2 at 305 °C. Additionally, FSP- Mn_3O_4 exhibited only slight change in soot oxidation activity after hydrothermal exposure at 750 °C and thermal aging at 1050 °C.

The practical efficiency of FSP- Mn_3O_4 was investigated by using a catalytic laboratory-scaled particulate filter. The TPO studies indicated that the major part of the soot deposited in the trap (ca. 80%) was weakly contacted to the catalyst causing oxidation above 400 °C only. Contrary, the minor fraction of tight contact soot evoked conversion already between 180 and 350 °C. This operation range indicated potential for the continuous regeneration of particulate filters in real diesel exhaust.

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1. Introduction

Diesel engines represent the most effective combustion motors and are therefore used for a broad range of technical applications,

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such as vehicles, locomotives, ships, working machines, cranes and power generators. The high efficiency of diesel engines benefits fuel economy associated with reduced emission of CO₂. However, a critical issue is the output of harmful soot particles. Diesel soot is carcinogenic [1] and contributes to the greenhouse effect [2]. Thus, emission thresholds were introduced and continuously tightened in the industrialised countries in the past. For the abatement of soot from engine exhaust, diesel particulate filters (DPF) are widely employed for vehicles and working machines since a couple of years. Particulate filters operate in the wall flow mode including the deposition of soot onto the porous filter walls, while the exhaust flows through them. But, as a result of soot filtration, the loaded DPF can cause backpressure potentially decreasing the engine efficiency. Hence, a regeneration step is mandatory to remove the soot deposits from the filter. For heavy duty diesels, the passive regeneration (continuously regenerating trap, CRT[®]) is applied, which involves the oxidation of the soot by using NO₂ and O₂ [3,4]. The required NO₂ is produced by the precious metal based diesel oxidation catalyst (DOC) positioned upstream to the DPF. As an alternative, the corresponding precious metals can be directly coated onto the particulate filter. However, in diesel passenger cars an active regeneration is additionally required due to the insufficient NO_x/soot ratio [5]. Thus, common strategies use the post-injection of fuel producing the emission of huge amounts of hydrocarbons, CO and H₂. These components are oxidised on the DOC resulting in steep temperature raise of the exhaust initiating the soot combustion [6]. Furthermore, fuel borne catalysts (FBC), e.g. cerium based organyls, are also employed for diesel passenger cars. FBC reduce the soot output of the engine and are embedded in the emitted particles thus enhancing the soot oxidation in the DPF [6].

Furthermore, catalytically coated diesel particulate filters (CDPF) aiming the activation of the soot/O₂ reaction are developed since many years. However, the efficiency of CDPF is related to tight proximity of soot and catalyst, whereas under practical conditions loose contact mostly predominates [7,8]. Thus, the soot oxidation catalysts known so far exhibit rather limited benefit upon real driving scenarios. A variety of catalytic materials, mainly transition metal oxides [9–17], mixed metal oxides [18–23] as well as rare earth metal oxides [27–36] were reported to be basically active in soot oxidation. Additionally, the promoting effect of alkaline metal oxides [37–41] was demonstrated.

Mechanistic investigations showed that the role of the catalyst in the soot oxidation is the transfer of oxygen from its surface to the soot. Three basic oxygen transport mechanisms are known for oxide catalysts. (1) In the surface redox mechanism, e.g. reported for Co₃O₄, surface oxygen of the catalyst is transferred at the interface to the soot, while the resulting vacancies of the catalytic surface are filled by gas-phase oxygen [12]. (2) The spill-over mechanism implies dissociative adsorption of oxygen on the catalyst, e.g. CeO₂ and Cr₂O₃, and subsequent transfer of the formed oxygen to the soot, whereas contact of both solids is not required [12,26]. However, it should be noted that for CeO₂ the oxygen migration by contact points additionally plays a crucial role [42]. (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; prominent examples are V₂O₅ and Fe₂O₃ [12,14].

Moreover, it has to be considered that the soot oxidation is a strongly exothermic reaction and as a consequence the local heat production also determines the kinetics. For instance, it was demonstrated that the evolution of reaction temperature can be buffered by the heat capacity of the catalyst. Thus, two opposite features exist when rising the amount of catalyst: on the one hand the number of contact points between catalyst and soot increases causing the acceleration of the soot oxidation, but on the other

hand the heat capacity also inclines, which inhibits the raise of temperature resulting in diminished increase in oxidation rate [43].

Furthermore, it should be stated that many oxide catalysts also enhance the direct soot/NO reaction to yield N₂ and CO_x. But, under oxygen-rich conditions the NO reduction represents rather a side reaction of the soot/O₂ conversion [13,44]. Also, it was recently reported that soot supports the NO_x reduction by NH₃ [45], whereas it inhibits the uptake capacity of NO_x storage reduction catalysts [46].

The goal of this work was to investigate the potential of manganese oxide catalysts for the soot oxidation pursuing the CDPF technique. Manganese oxides were taken as active component due to the efficiency of Mn based catalysts in the oxidation of soot [9,10,18,32,36], CO [47,48], NO [36] and CH₄ [49,50] as well as the selective oxidation of hydrocarbons [51,52]. In the present study, a couple of different manganese oxides were physical-chemically characterised and tested towards their soot oxidation activity to evaluate the importance of acid surface sites, specific surface area, particle size, reducibility and phase composition. For the assessment of the technical potential of the best catalyst, its thermal stability as well as performance under more practical conditions was investigated. Finally, isotopic studies with ¹⁸O₂ were performed to elucidate the role of the catalyst in the transfer of oxygen to soot.

2. Experimental

2.1. Preparation and physical–chemical characterisation of catalysts and soot

Mn₂O₃ and MnO₂ samples (>98%, Johnson Matthey) were commercially obtained, while Mn₃O₄ was synthesised according to the literature [53]. Furthermore, nano-sized manganese oxide was prepared by FSP using a bench described in detail elsewhere [54]. Briefly, an aqueous 0.5 M solution of Mn(NO₃)₂ · 4 H₂O (>98%, VWR) was mixed with iso-propanol in the volume ratio of 1:4 and was then sprayed and combusted via a two-substance nozzle (Duesen-Schlick). The nano-sized particles produced with a rate of ca. 3 g/h were collected on a sinter metal candle filter.

The characterisation of the catalysts was conducted by powder X-ray diffraction, scanning electron microscopy (SEM), temperature programmed desorption of NH₃ (NH₃-TPD), N₂ physisorption and temperature programmed reduction by H₂ (HTPR).

The PXRD analysis was made at room temperature on a D8 Advance diffractometer from Bruker AXS using Co-K α radiation (35 kV/45 mA) and a Goebel mirror. The diffractogram was recorded from 10° to 80° (2 θ mode) with a step width of 0.0164° and a time of 0.05 s per step. Quantitative phase analysis was carried out with TOPAS software (Bruker-AXS) including a standard fitting procedure according to the Rietveld refinement.

For NH₃-TPD, the sample was pressed to pellet at a pressure of 4 MPa, granulated and sieved to size of 125–250 μ m. Before TPD, the catalyst was pretreated in N₂ flow at 250 °C for 15 min. This was done to eliminate possible impurities, e.g. adsorbed H₂O, and to completely decompose nitrate species remaining from FSP synthesis as proven by preliminary TPD tests. Also, the pretreatment was made at 250 °C to avoid sintering of nano-sized particles. Subsequently, it was cooled to 50 °C and then the NH₃ exposure was started by adjusting a gas mixture of 500 vppm NH₃ and N₂ balance (Air Liquide). After saturation, the catalyst was flushed with N₂ and the temperature was linearly increased at a rate of 10 K/min. The total gas flow was maintained at 300 or 500 ml/min (STP). The temperature was monitored by a K-type thermocouple installed directly in front of the sample fixed by quartz wool. NH₃-TPD

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