



Photocatalytic carbon oxidation with nitric oxide



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ABSTRACT

The photocatalytic oxidation of carbon black on TiO₂ using nitric oxide as an oxidizing agent was investigated. Layer-wise deposited carbon and TiO₂ powder was illuminated with UVA light in the presence of NO at parts per million concentrations in dry and hydrated carrier gas at a temperature of 150 °C. Carbon was photocatalytically converted mainly into CO₂, and NO mainly into N₂. Carbon oxidation rates of 7.2 μg/h/mgTiO₂ were achieved in the presence of 3000 ppm NO. Under these experimental conditions in the absence of molecular oxygen, formation of surface nitrates causing TiO₂ photocatalyst deactivation is suppressed. Addition of water enhances surface nitrate formation and catalyst deactivation.

NO and carbon particulate matter are air pollutants emitted by diesel engines. Elimination of soot collected on a diesel particulate filter through oxidation is a demanding reaction requiring temperatures in excess of 250 °C. The present study opens perspectives for a low-temperature regeneration strategy for the diesel particulate filter that simultaneously performs DeNO_x reactions.

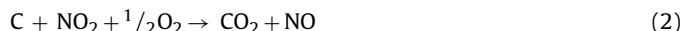
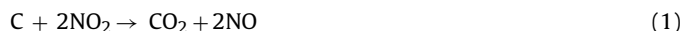
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1. Introduction

Particulate matter (PM) emissions generated in diesel engines have gained considerable attention due to the increasing number of diesel vehicles and due to their possible negative impacts on human health and environment [1–3]. There is increasing evidence on causal relationships between several diseases (e.g. cardiovascular and respiratory diseases) and chronic exposure to particulate matter [4,5]. The increasing concern has led to the introduction of more stringent exhaust emissions standards which necessitate the implementation of sophisticated exhaust gas purification systems in vehicles [6].

Currently, PM is removed from exhaust gas using a diesel particulate filter (DPF) [7]. PM trapped by DPF needs to be removed from the filter to avoid increasing backpressure which would degrade diesel engine performance. Periodic or continuous regeneration minimizes the risk of uncontrolled carbon burning in the filter [6]. Oxidation of retained PM to CO₂ in a diesel particulate filter is an evident way of filter regeneration. Oxidation of carbon using O₂ requires high temperatures of 500–550 °C [8]. Compared to O₂, NO₂ is a much more powerful oxidizing agent. In continuously

regenerated PM traps, NO emitted by the engine is oxidized to NO₂ over an oxidation catalyst positioned in front [8]. NO₂ is able to oxidize carbon at temperatures as low as 250 °C [9–13]. Reaction mechanisms of the oxidation of carbon by NO₂ in the presence of water vapor and molecular oxygen are well documented [12–15]. In the carbon oxidation reaction, the NO₂ molecules are reduced mainly to NO:



Since the DPF does not eliminate NO_x, an additional DeNO_x system needs to be implemented to eliminate the NO downstream of the DPF [16,17]. Reduction of NO_x using PM to N₂ instead of NO:



would eliminate the need of a separate DeNO_x system downstream of the DPF.

Selective formation of N₂ has been observed in the reaction of carbon with NO in the temperature range 600–1000 °C [18]. The formation of CO₂ and CO can be described globally by Eq. (3) combined with Eqs. (4) and (5) [19,20]:



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The simultaneous elimination of two pollutants, viz. carbon particles and NO via reactions (3)–(5) is attractive in view of automotive applications, but the very high temperatures required for these reactions are impractical. The temperature of diesel exhaust gas in latest generation vehicles remains below the 250 °C threshold for regeneration, especially during urban driving conditions [21]. Regeneration of a DPF often necessitates additional heating, which is achieved by combustion of fuel injected in the exhaust gas, representing a fuel penalty.

Photocatalytic processes could be an attractive alternative for accelerating depollution reactions at low temperature. Titanium dioxide is a popular photocatalyst for air as well as water treatment [22,23], because of the large band gap energy of TiO₂ materials (anatase: 3.2 eV, rutile: 3.03 eV) these materials can only be activated by UVA light [24]. Application of TiO₂ on surfaces for pollutant removal through a solar-driven photocatalytic oxidation process in air is well documented [25,26]. Visual evidence of lateral and remote oxidation of soot by UVA-irradiated titanium dioxide thin films has been reported [27]. The elimination process of carbon particles on outdoor surfaces at ambient conditions is however quite slow [28]. Chin et al. developed a kinetic model of photocatalytic soot oxidation and assumed two pathways of CO₂ formation [29,30]: a direct soot oxidation to CO₂ and a multistep reaction for CO₂ generation from intermediate species of unknown nature. The oxidizing species generated by the photoactivation process are assumed to be superoxide anions (O₂^{•-}) and hydroxyl radicals (HO[•]), derived from molecular oxygen and adsorbed water molecules, respectively [31–33]. Evidence from EPR and FTIR spectroscopy hinted at an essential role of molecular oxygen-related radicals in photocatalytic soot degradation [33]. Photocatalysis with TiO₂ has already been shown to be active in the reduction of NO_x using ammonia (photocatalytic selective catalytic reduction or, in short, photo SCR), and in ammonia oxidation [34,35]. To our knowledge, no reports are available on the use of photocatalysis for performing the oxidation of carbon using nitric oxide as an oxidizing agent under conditions relevant to engine exhaust purification.

We investigated photocatalytic oxidation of carbon black in the presence of nitric oxide and water over commercial TiO₂ catalyst. We found that carbon can be photocatalytically oxidized into CO₂ under varied conditions. Furthermore, most of the NO is reduced to N₂. Photocatalytic carbon oxidation with simultaneous NO_x reduction is an attractive concept for future photocatalysis-assisted exhaust after treatment systems.

2. Experimental

2.1. Materials and sample preparation

Commercial TiO₂ photocatalyst (Cristal Global Millennium PC500) was used. This TiO₂ powder consists of anatase, has a surface area of 350 m²/g and a primary particle size of 9 nm [36]. Printex U is a popular model carbon black for evaluating carbon oxidation catalysis [37]. An amount of 5 mg of Printex U was deposited on a glass plate (300 mm × 50 mm) by spreading and evaporating an isopropanol suspension. Subsequently, 50 mg of TiO₂ catalyst powder was spread over the soot-coated glass plate using isopropanol solvent as described earlier [35].

2.2. Reactor set-up

The glass plate supporting the carbon and TiO₂ layer was placed in a flat photoreactor (Fig. 1).

The thermostatic support made of stainless steel is temperature-controlled and can be heated to 200 °C. The sample was illuminated

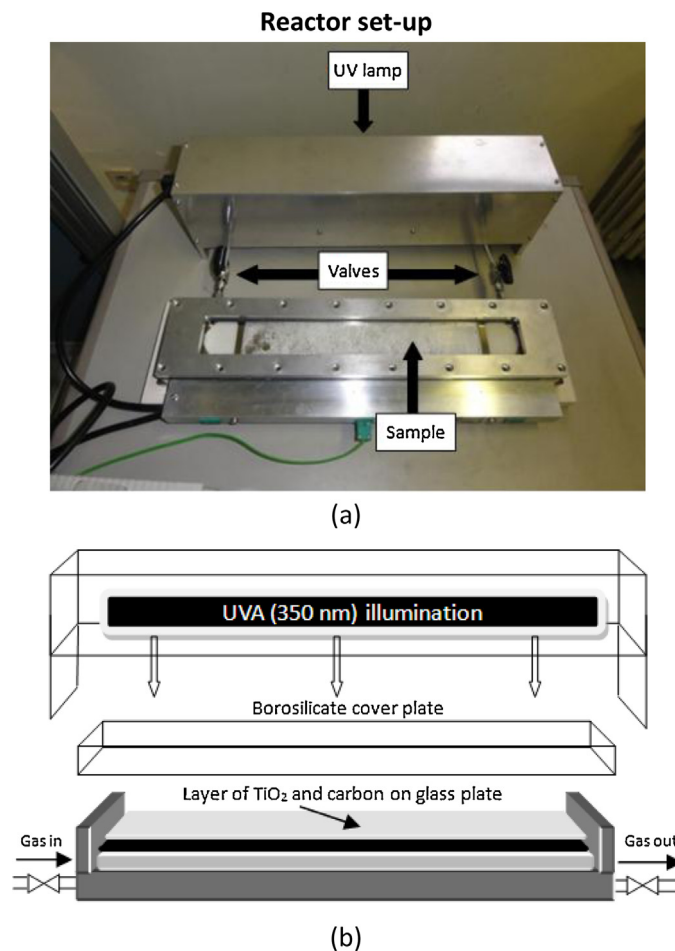


Fig. 1. Photograph (a) and schematic drawing (b) of the photoreactor.

from the top with a UVA-lamp (Rayonet) at a light intensity of 1.1 mW/cm². The UVA lamp is mounted in an aluminum housing covering the reactor block. Sealing of the reactor is done by a borosilicate glass plate (430 mm × 70 mm) and Viton O-ring (Eriks). The headspace between the glass plate with deposited sample and the borosilicate sealing plate is ca. 2 mm high, creating a gas volume of ca. 48 cm³. NO (5% in He) and N₂ are fed from gas cylinders using mass flow controllers (Bronkhorst). Water vapor is introduced in the N₂ stream via a temperature-controlled bubbler. Analysis of the gaseous reaction products is conducted via a UV detector for NH₃, NO and NO₂ (ABB Limas 11HW) and NDIR detector for N₂O, CO and CO₂ (ABB Uras 26 instrument). The detectors have specific filters for each gas compound, minimizing interference with other gases. After passing through the UV detector, the gas is led through an ABB SCC-C gas cooler for removal of water in the gas stream and lowering of the dew point to 3 °C. All corrosive components (SO₂, NH₃, NO₂) are transferred to the condensate for protection of the NDIR instrument. Both detectors are equipped with gas-filled cuvettes for autocalibration. The detection limits are less than 1% of the smallest measurement range (Table 1). The selectivity for N₂ was estimated from the nitrogen atom balance. Based on the detection limits, the standard deviation value was estimated at ±2% using the formula of cumulative uncertainty.

2.3. Carbon photocatalytic oxidation experiments

In a preliminary experiment, photocatalytic carbon oxidation was investigated under continuous flow of a gas mixture with 1000 ppm NO and 3% H₂O in N₂ at a flow rate of 150 ml/min,

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