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Photocatalysis assisted simultaneous carbon oxidation and NO_x reduction

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ABSTRACT

Photocatalysis assisted oxidation of carbon black was performed using TiO_2 photocatalyst under UV illumination in an atmosphere with NO, O_2 and water vapor at 150 °C. Carbon is oxidized mainly to CO_2 while NO is selectively converted to N_2. Enhanced O_2 and NO concentrations have a positive effect on the carbon oxidation rate. At a concentration of 3000 ppm NO and 13.3% O_2 in the gas phase the carbon oxidation rate reaches 2.3 $\mu g_{carbon}/mg_{TiO2}$ h, at a formal electron/photon quantum efficiency of 0.019. HR SEM images reveal uniform gradual reduction of the carbon particle size irrespective of the distance to TiO_2 photocatalyst particles in the presence of NO, O_2 and H_2O.

1. Introduction

Controlled oxidation of carbon nanoparticles is of interest to many practical applications. Regeneration of diesel particulate filters is a prominent example. A common filter regeneration strategy involves oxidation of the carbon deposit using NO_2 obtained by catalytic oxidation of NO emitted by the engine [1]. NO_2 mediated carbon oxidation proceeds at temperatures exceeding 250 °C, and NO_2 is reduced mainly to NO rather than N_2, necessitating an additional $DeNO_x$ system downstream from the filter [1]. In nanotechnology, oxidative modification of carbon nanomaterials is needed for selective elimination of amorphous carbon debris, and for altering physico-chemical properties such as enhancing hydrophilicity. To this purpose carbon nanotubes (CNTs) are oxidized with concentrated mineral acid (e.g. nitric acid and sulfuric acid) to facilitate dispersion in polar solvents [2,3]. Graphitic oxide obtained by oxidation of graphite with the mixture of strong oxidants (nitric acid, sulfuric acid or potassium permanganate) [4,5]. Improved methods have been reported, concentrated acid and strong oxidants are necessary for the oxidation process [6,7]. More sustainable chemical methods would be welcome [6].

Photocatalytic oxidation is mentioned among the green chemistry methods for sustainable development [8]. The method has been used to oxidize carbon, and for converting NO_x to N_2 various ways, and the possibility of combining both reactions has been suggested. Titanium dioxide is widely used for photocatalytic applications for its commercial availability and robustness [8]. UV light is needed for charge separation in TiO_2 semiconductor because of the large band gap of crystalline TiO_2 phases (anatase: 3.2 eV, rutile: 3.03 eV) [9]. Soot can be oxidized using sunlight-driven photocatalysis on TiO_2. Self-cleaning properties of TiO_2 coatings covered by soot have been demonstrated [10–16]. The efficiency of this photocatalytic process proceeding outdoors is, however, very low [10]. Oxidation of a 0.5 μm soot deposit requires e.g. 45 days [10,17].

NO_x elimination from air using photocatalysis is an emerging technology. Photocatalytic NO_x oxidation converts NO with O_2 to NO_2, which reacts further to nitrates that can be removed from the photocatalyst by water leaching. This $deNO_x$ concept has been implemented e.g. on the surface of concrete pavement [18,19]. Titanium dioxide which is photoactive under UV light achieves photodecomposition of NO to N_2 and O_2 [8]. The reaction is slow and inhibited by O_2. Substantial N_2O by-product formation is observed [20–22]. Modified TiO_2 and zeolites have been investigated to

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improve catalyst activity and N_2 selectivity of the NO decomposition reaction with some success [23]. Additionally, the photo-SCR activity of commercial and modified TiO_2 in the presence of sacrificial reducing agents such as NH_3, CO and short-chain hydrocarbon reductants has been demonstrated [24–32]. In nanotechnology, photocatalytic oxidation potentially is a sustainable method for the preparation of a variety of carbon materials such as oxidized carbon nanotubes and graphite oxide.

In a previous publication we reported that carbon black can be selectively photo-oxidized to CO_2 using NO in absence of O_2 [33]. Under those conditions in absence of O_2, NO was converted to N_2. The observed carbon oxidation rate was relatively low (ca. 2 $\mu g_{carbon}/mg_{TiO2}$ h). In this paper we investigate the potential of photocatalytic oxidation of carbon using reactive gas mixtures with ppm quantities of NO in addition to O_2. Promising results were obtained showing enhanced carbon oxidation rates and even oxidation of all carbon particles. Interestingly, NO is selectively reduced to N_2 even in the presence of O_2. The size reduction of carbon particles up on oxidation is monitored with HR SEM.

2. Experimental

2.1. Sample preparation

Millennium PC500 (Cristal Global) was used as TiO_2 photocatalyst. This photocatalyst has a high surface area of 350 m^2/g and a primary particle (not aggregates) size of 9 nm [34]. The carbon black material was Printex U (Evonik) considered as a synthetic mimic of soot [35]. An amount of 5 mg of Printex U was deposited on glass plates (430 mm × 70 mm) by spreading a suspension of Printex U in isopropanol. Samples were dried overnight at 120 °C. 50 mg of TiO_2 catalyst powder was deposited on the soot coated glass plate from an isopropanol suspension afterwards.

2.2. Photocatalytic reaction

The photocatalytic reaction was carried out in a home-made flat photoreactor [33]. The prepared sample was illuminated from the top with a UV lamp (Rayonet) at a light intensity of 1.1 mW/cm^2. Gases were fed from gas cylinders using mass flow controllers (Bronkhorst). More information concerning the experimental set-up and the gas analyzers can be found elsewhere [33]. The CO, CO_2, NO_x (NO & NO_2) and N_2O content in the reactor volume are analyzed after the illumination period using UV spectroscopy and NDIR (ABB Limas 11HW and Uras 26 gas analyzers). The photoreactor was operated in batch type experiments as follows. The reactor was purged first under a flow of dry N_2 gas at 150 °C for 30 min. Subsequently, the reagent gas mixture was sent through the reactor in absence of light. After reaching the desired NO_x concentrations (measured using the NO_x analyser at the outlet), the gas inlet and outlet were closed. At the end of an illumination period, the product gas mixture was conducted to the gas analysers using carrier gas.

2.3. Quantification of nitrates

Quantitative determination of nitrates was performed on spent catalysts which were scraped from the glass plate. Nitrates were dissolved by slurrying the scraped powder in deionized water. Solids were removed by filtration. Dissolved nitrate was determined using a Hach Lange LCK 339 or 340 test kit. The conversion of NO to N_2 was determined from the N-atom balance over the reactor.

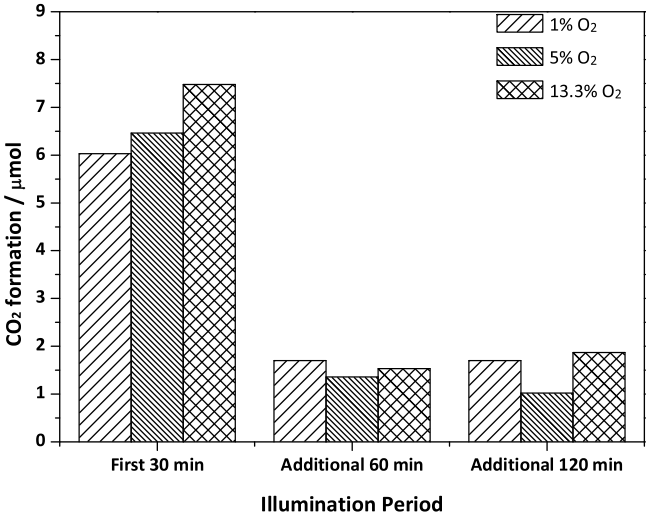

Fig. 1. CO_2 formation in photocatalytic oxidation of carbon black in presence of TiO_2 in a gas mixture with varied O_2 concentration and 3% H_2O.

2.4. Fourier transform infrared (FTIR) measurements

Fourier Transform Infrared (FTIR) spectra of scraped powder diluted in KBr (0.5 mg in 473 mg KBr) were recorded on a Bruker IFS 66 v/s.

2.5. High-resolution scanning electron microscopy (HR SEM) measurements

HR SEM images were recorded using low accelerating voltages (2 kV) with a Nova NanoSEM450 (FEI) equipped with BSE detectors, Concentric Backscattered detector (CBS), Through Lens Detector (TLD) combined with a beam deceleration mode (utilizing a stage bias up to 4 kV). The layer of carbon black and TiO_2 was deposited on an aluminium plate and imaged before and after carbon photo-oxidation. SEM images were taken on samples as such without any further modification.

3. Results and discussion

Printex U is commonly used as a model carbon material for investigating kinetics of carbon oxidation processes [36]. It is considered to be a good model for the elemental carbon portion of particulate matter emitted by diesel and gasoline direct injection engines [37,38]. A layer of 5 mg carbon black covered by 50 mg TiO_2 was exposed to UV light in a closed flat-plate photoreactor filled with gas mixtures containing 3% H_2O and O_2 at three different concentrations (1%, 5% and 13.3%). The reaction proceeded very slowly at room temperature and was accelerated upon heating. A reaction temperature of 150 °C was selected. The gas composition in the reactor was analyzed after illumination for 30 min. New gas was introduced and illumination continued for 60 min. The procedure was repeated for a third 120 min illumination period. The obtained photocatalytic oxidation of carbon to CO_2 is presented in Fig. 1. CO was always formed in much smaller quantities than CO_2 (typically only about 2% of the oxidized carbon, see Supporting information). Much more CO_2 was formed in the first illumination period compared to the second and third period. Increasing the O_2 concentration enhanced CO_2 formation especially in the first run. Printex U type carbon black contains a variety of carbon species including easily oxidized oxygenated groups [39]. This carbon fraction is oxidized first [37]. Refractory carbon representing the main share of carbon black is more difficult to oxidize [40–42]. Photocat-