



Improved photocatalytic ozone abatement over transition metal-grafted titanium dioxide

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ABSTRACT

Photocatalysis can be an effective means to combat air pollution. Up to now, mainly direct NO_x abatement has been studied, but ozone abatement could also contribute significantly to improved air quality. The ozone decomposition rates of different commercial titanium dioxide based photocatalysts grafted with copper, manganese or iron ions were studied both under UVA illumination and under dark conditions. Copper and manganese grafting were effective in significantly increasing the ozone decomposition rate of the photocatalysts. The procedure worked best when using low surface area pigmentary anatase rather than nanoparticulate photocatalysts. Manganese grafting also increased the ozone abatement under dark conditions, likely due to small MnO_x clusters acting as catalysts. Iron grafting appears to be the most universal method of improving the photocatalytic ozone removal rate, as it worked for all four different photocatalysts studied. Extremely low iron grafting ratios of 0.002 at.% were sufficient to dramatically improve the performance.

1. Introduction

The air we breathe is one of our most precious resources. Yet it is often contaminated with dangerous pollutants, endangering our well-being and health. Current studies estimate about 3.3 million premature deaths per year on a global scale as a direct consequence of air pollution [1]. In modern industrialized countries such as in North America or Europe, air pollution is typically only a problem in terms of ultrafine particles and nitrogen dioxide. However, especially the latter is a very pressing concern, for instance in Europe, the existing limit values of 40 µg m⁻³ are frequently exceeded in many urban areas [2]. It has also been shown that despite significant advances in exhaust treatment technology, emission standards and more restricted traffic rules, the NO₂ levels have been virtually unaffected and are still about where they were 20 years ago [2]. When considering NO_x based air pollution, ozone should always be considered as well. Most of the NO₂ present in urban air is not emitted directly but formed by oxidation reactions, typically with ozone. It has been pointed out that significant reductions in the NO₂ levels can only be expected when NO_x levels are drastically reduced or when the ozone background concentration can be lowered [2].

Ozone itself typically does not present a significant problem in urban areas owing to its high reactivity with the high concentrations of NO_x present. While there often is an ozone background of several tens of ppb, it is typically not observed in that magnitude and mostly present

in the form of NO₂ which is formed by reaction of ozone and NO, reaction (1) [2]. However, as described by the Leighton equilibrium, some of that NO₂ photolyzes back to NO and O₃ during daytime, reactions (2) and (3) [3].



Due to these reactions, each molecule of ozone that can be decomposed effectively equals one NO₂ molecule that is not formed out of NO in the first place. Therefore, ozone abatement can be considered as an indirect way to reduce ambient NO₂ levels. Also, in more rural areas with very low NO_x levels, ozone can present a significant problem as it is not immediately quenched by NO and can therefore reach dangerous concentrations. The air quality in those areas would also greatly benefit from a reduced background ozone level.

Heterogeneous photocatalysis has been studied intensively in the last decade as a means to combat air pollution [4–11]. Due to their exceptional material properties, titanium dioxide based photocatalysts can easily be incorporated into various construction materials such as concrete, paving stones, paints, windows or roof tiles. There, owing to their photocatalytic properties, they are able to mineralize various air pollutants such as NO_x or VOCs. However, direct NO_x abatement on titanium dioxide is quite challenging as the reaction involves several

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toxic intermediates which may be released in the process [12]. Also, oxidation rates of NO are typically much higher than for NO₂ so that while NO is often reduced to a significant extent, the impact on NO₂ is far smaller [13,14]. Additionally, the photocatalyst suffers from nitrate poisoning, which accumulates over time until it is washed off by rain [15]. This can lead to significant deactivation in longer dry periods. Depleting ozone instead of or in addition to direct NO₂ abatement has the advantage that it is completely traceless and does not induce nitrate poisoning as it is the case with NO_x oxidation. While not having an instantaneous direct impact on the NO₂ levels, a reduced ozone background will lead to less NO₂ formation over time, which presents an effective indirect NO₂ reduction process.

It has been shown in 1981 by González-Elipse and co-workers that ozone can be photocatalytically degraded on illuminated titanium dioxide surfaces [16]. As evidenced by EPR spectroscopy, the reaction proceeds both *via* the reductive route (reaction (4)), forming O₃^{•-} and also *via* the oxidative route (reactions (5) and (6)), forming O₄^{•-} [16]. Both of these short-lived intermediates readily decompose to form O₂ and O₂^{•-} (reactions (7)–(9)) [16]. The latter (superoxide) is also helpful in the general context of air pollution control as it can directly react with NO to form nitrate on the photocatalyst surface, whereas the direct reaction of NO with ozone would produce the toxic NO₂.



However, up to now, photocatalytic ozone abatement for the purpose of environmental air pollution control has been largely neglected in favor of direct NO_x abatement. Only few studies exist which report on the photocatalytic ozone abatement properties of titanium dioxide [16–20]. This is partly due to the poor efficiency for ozone decomposition of unmodified titanium dioxide. However, as this study will show, the efficiency can be dramatically improved by simple and inexpensive methods, so that ozone decomposition can be an important contributor to the overall air depollution properties of the photocatalyst.

In this study, we explored the strategy of transition-metal grafting to increase the ozone-photo-degradation rate of titanium dioxide based photocatalysts. In this procedure, which has been reported to enhance the UVA as well as the visible light activity of many photocatalysts, transition metal ions are strongly adsorbed onto the host crystals where they form small isolated ions or clusters which improve charge carrier separation and electron transfer kinetics [21–32]. However, up to now, this technique has not been studied as a means to improve ozone degradation over titanium dioxide.

2. Experimental details

The photocatalyst powders were received from Evonik (Aeroxide P25), CristalGlobal (CristalAcTiV PC105) and Kronos (K7050 and K1001) and used as received. Iron(III)chloride hexahydrate (Alfa Aesar), manganese(II)chloride dihydrate (Merck), copper(II)chloride dihydrate (Alfa Aesar) and hydrochloric acid (Merck) were used as received. Unless otherwise stated, water refers to deionized water (> 10 MΩ cm).

For the preparation of the grafted materials, a procedure developed by Irie et al. was adopted [22]. First, a solution of the respective chloride salt of the grafting element was prepared where the concentration would reflect the desired final concentration on the photocatalyst. For iron grafting, the solution was acidified to pH2 using

hydrochloric acid. Into this solution, 100 g L⁻¹ of the photocatalyst was suspended and stirred for one hour in a sealed container at 90 °C. After cooling to room temperature, the suspension was filtered, washed with copious amounts of water and finally dried at 110 °C for 24 h. The resulting powders were ground in an agate mortar and then used in this form. An aliquot of the filtrate was collected for ICP-MS analysis to determine the amount of residual, *i.e.*, not adsorbed, metal ions. From the difference of the total added amount and the residue in the filtrate, the theoretical grafting amount is calculated. The “washed” samples were prepared analogously, just without adding any metal salt.

The ozone abatement was measured in a modified setup for photocatalytic NO_x abatement according to the international standard ISO 22197-1 [33]. The ozone was prepared using an electrical discharge ozonizer (innotec high engineering GmbH, Germany) operated with pure oxygen in order to not produce any NO_x. The ozone gas stream was diluted by both a dry and wet synthetic air stream and made up to 50% relative humidity, about 1 ppm ozone and 3 L min⁻¹ flow rate. This test gas mixture was then passed through the photocatalytic reactor made out of PEEK which comprises a sample holder with the dimensions of 5 × 10 cm², in which a sample holder containing the photocatalyst powders was placed. Approximately 2.8 g of the photocatalyst powders was uniformly dispersed on the sample holder and slightly pressed on with a flat plunger to form a uniform flat surface. The sample holder is illuminated from above through a UVA transparent cover glass by a 365 nm UVA-LED-array (Omicron Laserage Laserprodukte GmbH, Germany) which is calibrated to deliver an irradiance of 10 W m⁻² at the sample surface. The gas stream is passed above the sample through a 5 mm high slit that is regularly reduced to 1 mm by turbulence barriers, which was reported to improve mass transfer (see Ifang et al. for details) [34]. All tubing and connections were made of polymers to avoid metal surfaces which could catalytically decompose ozone. The resulting gas stream was analyzed using an environmental ozone analyzer (Horiba APOA-370). The relative ozone abatement was calculated by the relation of removed ozone to initial ozone (measured in a reactor bypass). Each experiment was performed until steady state conditions were achieved and then the concentration was averaged over 20 min in the steady state conditions in order to achieve a sufficiently high precision.

Nitrogen adsorption-desorption isotherms were measured with an Autosorb iQ (Quantachrome GmbH & Co. KG, Odelzhausen, Germany). The samples were activated at 250 °C under vacuum for 16 h. The measurements were performed at -196 °C by taking measuring points between 0.02 to 1 P/P₀. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation from a linearized isotherm equation between 0.03 and 0.25 and the total pore volume at P/P₀ = 0.995.

3. Results

Four different commercial titanium dioxides were studied. The first is the widely used Evonik Aeroxide P25 powder which is a mixture of both anatase and rutile phases and a surface area of about 50 m² g⁻¹. Also, a pure anatase photocatalyst (K7050) and a pigmentary grade anatase (K1001) from Kronos were studied as a comparison. The former has a large surface area of more than 300 m² g⁻¹ and the latter a very small one with about 10 m² g⁻¹. Finally, some experiments were also conducted with CristalGlobal CristalAcTiV PC105 photocatalyst which consists of anatase particles with a surface area of about 90 m² g⁻¹. These photocatalysts were grafted with copper, manganese and iron ions in the concentration range of 0.0001 at.% (1 ppm) to 1 at.%. The actual amount of grafted ions was determined indirectly by taking the difference of added metal salt and subtracting the residue found in the filtrate as analyzed by ICP-MS. In most cases, it was found that the majority (> 80%) of metal salts were grafted onto the TiO₂ surface.

No evidence for a change in the crystal phase or particle size was observed in XRD or SEM/TEM analysis (not shown). However, the

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