Development of Unconventional Photocatalytic Reactors and Processes for the Abatement of Harmful *N*-containing Pollutants

Ilenia Rossetti[a*], Matteo Compagnoni[a], Gianguido Ramis[b], Francesca Freyria[c],
Marco Armandi[c], Barbara Bonelli[c]

[a] Dip. Chimica, Università degli Studi di Milano and INSTM Unit Milano-Università, Milan, Italy
[b] Dip. Ing. Chimica, Civile ed Ambientale, Università degli Studi di Genova and INSTM Unit Genova, Genoa, Italy
[c] Department of Applied Science and Technology and INSTM Unit of Torino-Politecnico, Politecnico di Torino, Turin, Italy
ilenia.rossetti@unimi.it

In the present work, innovative photocatalytic processes were developed for the abatement of harmful N-containing compounds, focusing on selectivity towards innocuous N_2, to be applied for the treatment of waste waters to meet legislative specifications.

The photocatalytic performance of the samples has been checked for the photoreduction of nitrate ions, the photooxidation of ammonia and of organic N-containing compounds. Catalytic performance was correlated with the properties of the nanomaterials. Two innovative semi-batch photoreactors were specifically designed and optimized for this application.

Different photocatalysts have been compared. TiO_2 has been prepared in nanosized form by using an innovative flame pyrolysis (FP) approach, able to synthesise in one step single or mixed oxide nanoparticles, characterized by homogeneous particle size and good phase purity. In some cases Pd has been added to TiO_2 by post synthesis impregnation. The role of the metal nanoparticles was the enhancement of the lifetime of the photoproduced charges by electron trapping. The same materials formulations have been prepared starting from commercial nanostructured TiO_2 supports for comparison purposes. The addition of Pd revealed the key to improve both the conversion and the selectivity to N_2. The FP prepared materials were in general more active than the commercial TiO_2 P25 sample.

1. Introduction

The World Health Organisation recommended levels of nitrates, nitrite and ammonium concentration in drinking water to be 50 ppm nitrate, 3 ppm nitrite and 0.5 ppm ammonium. A further restriction was set to 10 mg/L for nitrates in drinking water by the US Environment Protection Agency. Such limits are hard to respect through the current technologies, and this possibly affects the health of *ca.* 25 million people in the US (Burow et al., 2010), making nitrates the most ubiquitous contaminant in drinking water sources (Nolan et al., 2010). As well, ammonia is one of the major N-based pollutants in wastewater. It contributes to eutrophication (Lee et al., 2002) and is toxic even at very low concentration for human and animal living species. Common methods for NH_4^+/NH_3 removal are based on biological nitrification, stripping, breakpoint chlorination and ion exchange, but each of them is characterised by disadvantages. For example, the efficiency of biological treatment is highly dependent on temperature, dissolved oxygen, the carbon source, pH, and the concentrations of toxic substances (Christensen & Harremoes, 1978).

The economic impact of nitrogen-based pollution for the EU-27 is safely estimated between €25 billion and €115 billion per year, reaching almost triple value when taking into account also other strictly correlated phenomena.

Among the removal methods, biological processes are generally regarded to be the most efficient. However, they present disadvantages, including handling difficulties and large equipment requirements. Moreover, they are difficult to apply to treatment of wastewater that contains harmful co-existing species for bacteria.

Therefore, the development of cheaper and easily scalable systems for their abatement is more than welcome. This relevant topic has been recently reviewed concerning both the removal of inorganic N-containing pollutants (Compagnoni et al., 2017) and organic contaminants such as azo-dyes, drugs and pesticides (Freyria et al., 2017).

In this work, we propose photocatalytic process for the reduction of NO_3^- and the oxidation of ammonia. In both cases the goal is to achieve the highest possible selectivity towards innocuous N_2. The set up of a new, scalable photoreactor is described, together with the photocatalytic activity for both reactions of nanostructured catalyst prepared by flame pyrolysis.

2. Experimental

2.1 Catalysts preparation

A commercial sample of TiO_2 P25 (Evonik) was used as reference material. It is a mixture of 20 % rutile and 80 % anatase, prepared in nanostructured form, with a specific surface area *ca.* 50 m^2/g.

TiO_2 was also prepared in nanostructured form by means of a home-made flame pyrolysis apparatus (FP). This method is suitable for the continuous one-step preparation of single or mixed oxides and is described in detail elsewhere (Chiarello et al. 2007). The frame pyrolysis apparatus includes a nozzle burner, which is co-fed with oxygen and with an organic solution of the oxide precursors. The organic solvent acts as fuel for the flame, whereas oxygen is the comburent and the dispersing agent. The TiO_2 sample was prepared from a solution of Titanium(IV)-isopropylate (Aldrich, pur. 97 %) in xylene, with a 0.67 M concentration referred to TiO_2. The burner was fed with a flow rate of 2.2 mL/min of the solution and 5 L/min of O_2. The pressure drop across the nozzle was set to 1.5 bar.

In case, Pd was added as co-catalyst with a 0.1 wt% concentration by wet impregnation from a solution of $Pd(NO_3)_2$.

2.2 Photocatalytic tests

Photocatalytic reduction of NO_3^- and oxidation of NH_3/NH_4^+ in water were carried out in a specifically designed Pyrex reactor. The catalysts were suspended in an aqueous solution of NH_4Cl (0.2M) or $NaNO_3$ (0.006M) and the suspension was stirred using a magnetic stirrer. The typical photocatalyst concentration was 1 g/L, based on preliminary screening. The reaction suspension was thoroughly degassed and then exposed to He. The reactor was operated in semi-batch mode: the solution containing the pollutant to be photoconverted was added at the beginning of the reaction in batch mode, whereas a gas stream continuously flowed through the reactor. The gas was composed by He during the conditioning-outgassing phase preliminary to every measurement. He was fed in continuous mode also during the nitrate photoreduction tests, whereas it was substituted by synthetic air (80 vol% He + 20 vol% O_2) during the ammonia photooxidation experiments. In both cases, the N_2 produced was continuously removed from the reactor. A trap for ammonia, possibly stripped from the reactor, was placed downstream.

A medium-pressure Hg vapour lamp was placed on the top of the photoreactor with a measured specific power of 69.5 W/m^2 and emitting in the wavelength range 254 - 364 nm.

The reactor temperature was kept at 298 K by cooling water circulating in a properly designed cooling jacket around the photoreactor.

The evolved gas was analysed on-line by gas chromatography (Agilent, mod. 5980, He was used as carrier gas) equipped with two columns connected in series (MS and Poraplot Q) and with a thermal conductivity detector (TCD).

Ammonium/ammonia was determined through a Perkin Elmer Lambda 35 UV-Vis spectrophotometer, following the Nessler method at a wavelength of 420 nm.

The concentrations of NO_3^-, NO_2^-, and possibly other interesting anions were determined by using a ion-chromatograph (Metrohm, 883 Basic IC plus).

In a typical run, system outgassing was carried out for *ca.* 1 h by flowing He and analysing the outflowing gas by gas chromatography until elimination of O_2 and N_2. After conditioning, a first sampling allowed to determine the initial concentration of the reactant, then irradiation started and repeated sampling was carried out each hour. Conversion and selectivity were calculated as follows:

$$Conversion\ i\ (\%) = \frac{(n_i^\circ - n_i(t))}{n_i^\circ} \times 100 \qquad i = reactant \tag{1}$$

$$Selectivity\ j\ (\%) = \frac{n_j}{v_j(n_i^{\,\circ} - n_i(t))} \times 100 \qquad j = product;\ v = stoich.coeff. \qquad (2)$$

3. Results and discussion

3.1 Set up of the testing rig

A first experimental set up was tested for both the ammonia photooxidation and the nitrates photoreduction reactions. The reactor was irradiated externally from the topside, which was closed through a quartz window, transparent in the UV-Vis range of interest. The sketch of the reactor is reported in Figure 1.
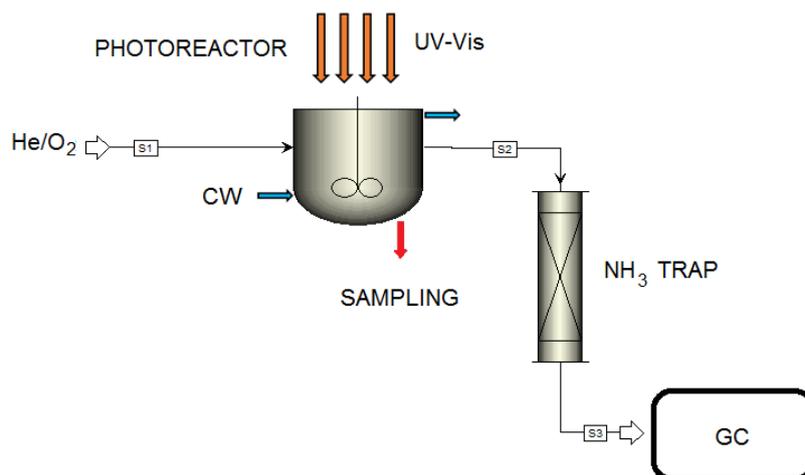

Figure 1: Sketch of the photoreactor used. CW = cooling water.

A semi-batch reactor configuration was adopted, with a gas stream constituted by 20 vol% O_2 in He continuously bubbling in the ammonia-containing suspension of the photocatalyst during the photo-oxidation process, whilst only He was used during the nitrate reduction tests. In the former case one of the reactants was fed in batch mode (ammonia), oxygen continuously, and one of the products, molecular nitrogen, was continuously removed. It should be underlined that the use of He is here suggested in order to evaluate the formation of N_2 as product. Once the process is optimized, air and N_2 are considered for scalu-up. The possible over-oxidation byproducts, nitrates and nitrites, were kept in the photoreactor, thus allowing their possible combined post treatment. Similar approach was adopted during the tests for the photoreduction of nitrates, where the reactant, sodium nitrate, was fed in batch mode, whereas the desired product (N_2) was continuously withdrawn, leaving in the reactor the possible over-reduction product, *i.e.* ammonia/ammonium.

This set up also allowed to quantify the selectivity to the desired product, nitrogen, using a simulated air in the case of ammonia photoxidation and pure He during the photoreduction experiments. This is a very challenging point. Indeed, usually the selectivity to N_2 is evaluated from N-balance, after quantification of nitrate, nitrite and ammonia and neglecting possible other intermediates (e.g. nitrosoamines, which are substances of concern) (Ren et al. 2015).

The external lamp was placed on the top of the photoreactor in order to simulate a future application directly by sunlight. This configuration allows easier scale up with respect to reactor configurations based on immersion lamps sometimes found in the literature, which have the advantage of closer (and thus more efficient) irradiation of the reacting suspension, but are not easily feasible for scale up, especially if the final scope is the use of sunlight. In the present configuration with external lamp, the correct exposure of the photocatalyst to the light source should be optimised by improved reactor geometry (proper height/diameter ratio) and appropriate mixing of the suspension. Testing on different photoreactors geometries and fluid-dynamic modeling are currently in progress to optimise this point.

Another issue is the possible stripping of ammonia (reactant or product) by the flowing stream, depending on pH. Of course, this may prevent reliable ammonia quantification, but it can also damage the GC columns when an online GC is used, as in the present case. In order to cope with both issues we have placed a downstream removable ammonia trap. In a first design, the gas stream was sent to an absorption column, filled with diluted H_2SO_4. The solution was titrated at the end of each test to quantify the possibly stripped

ammonia. This configuration induced an excessive pressure drop to allow the further inlet of the gaseous stream to the online GC, therefore the absorption system was substituted with an adsorption bed, filled with zeolites in acidic form. The possibly stripped ammonia was quantified in this case by temperature programmed desorption (TPD) up to 800°C at the end of the test. The ammonia possibly released was quantified through a TCD detector. During system set up we performed different testing by varying the gas flowrate, the pH of the solution and ammonia concentration in the photoreactor. We never detected ammonia transported downstream by stripping with both traps configurations. Therefore, in the final design we kept the adsorption trap containing zeolites as a guard bed, only.

3.2 Photocatalytic tests

A preliminary set of activity tests for both reactions have been carried out on bare titania photocatalysts. This semiconductor was chosen considering its well known photoactivity and photoresistance towards corrosion (Ohtani et al. 2010). In particular, we compared the performance of a FP-prepared catalyst with the commercial P25 benchmark. The activity of the catalysts for the photoreduction of ammonia is reported in Figure 2.
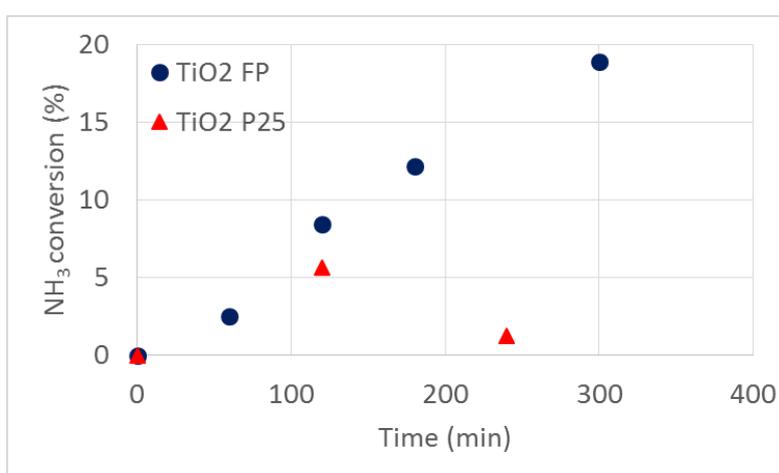

Figure 2: Ammonia conversion versus time. Selectivity 100 % to N_2.

The TiO_2 sample prepared by FP exhibited higher activity with respect to the commercial sample, reaching ca. 20 % conversion after 5 h, without indication of decay or deactivation. By contrast, the commercial sample was less active and most of all its activity was rapidly ruled out. Some induction period was observed, due to the need of sample conditioning upon irradiation. The most interesting point is that no trace of nitrites or nitrates was observed, confirming a full selectivity to the desired product, i.e. molecular N_2.
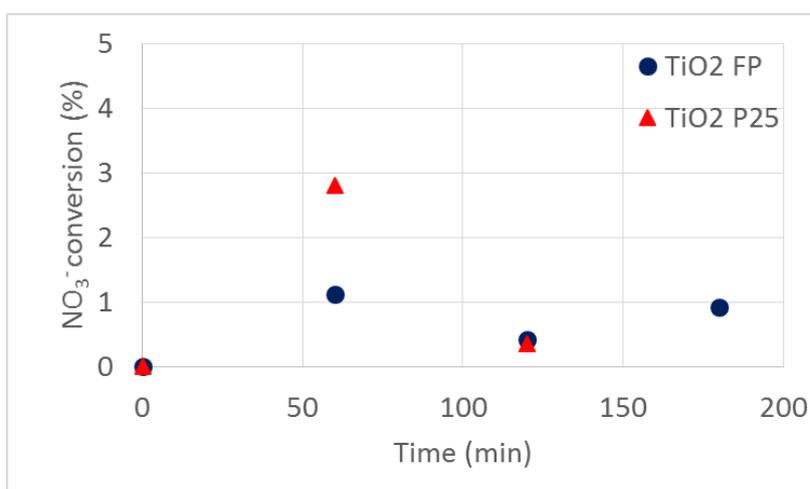

Figure 3: Nitrate conversion versus time. Selectivity 100 % to NH_3.

Additionally, we tested the catalysts for the photoreduction of nitrate. The results are reported in Figure 3. The activity in this case was lower and selectivity was 100 % to ammonia, a highly undesired by-product. Moreover, competitive reactivity was observed among the two reactions. Indeed, as soon as ammonia started to form, it was oxidised back to nitrate with decreasing conversion. The problems to be solved are two, one related to catalyst formulation, in order to enhance its activity and selectivity, the other related to process design, through the addition of a hole scavenger such as and organic compound, easier to oxidise with respect to ammonia. In the following we will deal only with the former issue due to the required brevity of this communication.

Pd was added in very small amount to the FP-prepared catalyst. Its activity and selectivity during the photoreduction of nitrate are reported in Figure 4. One order of magnitude higher nitrate conversion was achieved upon the addition of a very small amount of Pd, without formation of nitrite and much more limited selectivity to ammonia, which became a secondary byproduct, although still too relevant.
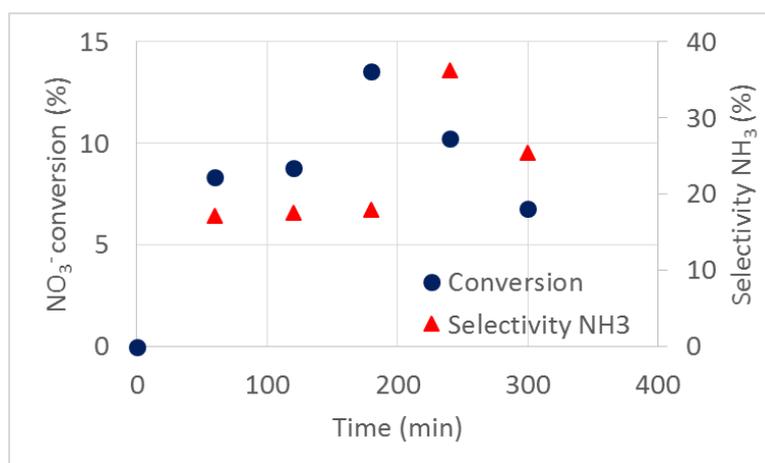

Figure 4: Nitrate conversion and selectivity to NH$_3$ versus time. Catalyst composition: 0.1 wt% Pd/TiO$_2$ prepared by FP.

Based on these results and given the full selectivity to N$_2$ during the photooxidation of ammonia, a two step process may be conceived, with the photoreduction of nitrates (and nitrites) as a first stage, followed by the photooxidation of the originally present and newly formed ammonia.

4. Conclusions

A photoreactor has been set up allowing to achieve the photoreduction of nitrates and the photooxidation of ammonia in semibatch mode. Its configuration, to be further optimised as for geometry and mixing, is suitable for scale up, easily implements immobilised photocatalysts and is ready to use with direct sunlight. These first results on both reactions let us conclude that the flame pyrolysis procedure is a viable technique for the preparation of either bare or metal-doped semiconductors in nanosized form, to be used for the photocatalytic abatement of inorganic N-containing pollutants in waste or drinking waters. Even if a photoreactor with external irradiation is less efficient than one base on immersion lamps, it is much more suitable for scale up and most of all for the direct application with solar light. Sufficiently high ammonia conversion was achieved during photooxidation in semibatch configuration, up to *ca.* 20 % after 5 h, with 100 % selectivity to N$_2$.

The same undoped catalyst was much less active during the photoreduction of nitrate, requiring the addition of a small amount of Pd to achieve suitable conversion (*ca.* 14 % after 3 h, with less than 20 % selectivity to NH$_3$). The addition of the noble metal also allowed to improve the selectivity to N$_2$, limiting the undesired formation of ammonia, which was instead the only product observed with the undoped titania catalysts. According to these results, a two step process may be designed, achieving the full removal of nitrates and subsequently oxidising ammonia with 100 % selectivity to N$_2$.

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