Photooxidation of NO and NO_2 with TiO_2-Based Materials

Silvia Suárez, Alberto E. García de Castro, Mario Escobar, and Benigno Sánchez

Abstract The high level of NOx in the air of urban areas is a major problem. NO_2 is one of the main pollutants found in big cities. Photocatalysis has been proposed as a remediation technology to control the NOx emission. Nevertheless, efforts are focused on the treatment of NO instead of NO_2. In this communication, we have analyzed the photocatalytic performance of TiO_2-based materials with different textural and chemical properties for the photocatalytic oxidation of NO and NO_2. The effect of photocatalyst loading, residence time, and relative humidity was studied in order to achieve the optimum photocatalytic performance. The results presented in this work indicate the importance of these parameters to obtain high photocatalytic efficiencies.

Keywords TiO_2 · NOx photooxidation · Photocatalysis · ISO 22197-1:2007

1 Introduction

The high level of air pollutants in urban areas is a major concern for today's society. NO_2, particulate matter ($PM_{2.5}$ and PM_{10}) and tropospheric O_3 are among the most harmful contaminants, responsible for severe environmental problems and causing pulmonary and other diseases in the population [1]. Among these pollutants, special attention was focused on NOx. Generally, the term NOx refers to both NO and NO_2, the main nitrogen oxides emitted by anthropogenic sources. Moreover, nitric oxide is easily oxidized to nitrogen dioxide in the presence of sunlight and oxygen. NOx are responsible for important damage to the environment, such as the nitric acid rain and the formation of the photochemical smog. The latter is produced by the reaction of NOx with volatile organic compounds (VOCs) in the presence of sunlight, resulting in

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a highly oxidant atmosphere. Photocatalysis is a well-established Advanced Oxidation Process, for the elimination of pollutants in the air [2]. The control of NOx concentration in urban areas by this technology is currently attracting the attention of both scientific community and infrastructure-engineering companies [3]. Most studies found in the literature deal with the photocatalytic performance of construction materials based on TiO_2 for NO photooxidation. Nevertheless, the main NOx pollutant found in the urban air, and responsible for traffic restriction is the NO_2. Then, a study of the photocatalytic performance of TiO_2 with different textural and crystal structures for both NO and NO_2 photooxidation reactions is required. In this communication, we analyzed the photocatalytic performance of some of the benchmark commercial TiO_2 (P25, TiO_2-G5, TiO_2-rutile and TiO_2-NP, Kronoclean 7000) for the photocatalytic degradation of NO under the ISO 22197-1:2007 standard. Moreover, the NO_2 photooxidation reaction studies were carried out modifying the conditions reported in the ISO. The effect of the photocatalytic loading, the residence time, and the relative humidity on the photocatalytic performance was analyzed. Textural and chemical properties of the materials (N_2 adsorption–desorption, UV–Vis, XRD, surface net charge) were studied in order to establish a sensible relationship between physico-chemical and photocatalytic properties.

2 Materials and Methods

Commercial samples TiO_2-P25 (Ti-P25, Evonik), TiO_2-G5 (Ti-G5, Crystal), and Kronoclean 7000 (Ti-KC, Kronos) were studied. TiO_2 nanoparticles (Ti-NP) was synthesized by the preparation of a TiO_2 sol, as previously reported [4]. All samples were heat treated at 500 ºC/3 h. TiO_2-rutile particles were prepared by calcination of TiO_2 at high temperature. The surface area of the materials was analyzed by N_2 adsorption–desorption (ASAP 2420), the band-gap energy by UV–Vis spectroscopy (Lamba 650 UV–Vis PerinElmer), the net surface charge by microelectrophoresis laser Doppler (Zetasizer Nano ZS90) and the crystal phases by XRD (PANalytical X'Pert PRO). Moreover, TiO_2 samples were analyzed by FTIR before and after the photocatalytic reaction by the preparation of KBr pellets (FT-IR Thermo Nicolet 5700). Photocatalytic activity measurements for NO photooxidation were performed under ISO 22197-1 (total flow F = 3000 mL min^{-1}, [NO] = 1000 ppb, R.H. = 50%, UVA I = 10 mW m^{-2}, reaction time = 300 min) [5]. Samples of 10.0 × 5.0 cm^2 were used in a reactor with the dimensions detailed in the standard. The TiO_2 powders were immobilized on borosilicate glass used as substrate. The effect of the photocatalysts amount for the NO photooxidation was studied incorporating different photocatalysts loading, between 1.5 and 6.0 mg cm^{-2} onto the substrate. Moreover, experiments for the degradation of NO_2 were carried out under similar conditions as for NO, using only 500 ppb NO_2. The reaction time under UV-A was set to 120 min and the other parameters were kept the same as described in the ISO 22197-1:2007. The effect of the residence time was studied at a total flow of 1500 mL min^{-1} and 3000 mL min^{-1}. Finally, the influence of the relative humidity

Table 1 Different titanium dioxide samples analyzed treated at 500ºC and photocatalytic performance for NO and NO_2 photooxidation (3.0 mg cm^{-2})

Samples	TiO_2	BET area $m^2\ g^{-1}$	Eg eV	NO_e[1] μmoles[1]	NOx_e	NO_{2p}	NO_{2e}[2] μmoles
Ti-P25	P25	49	3.0	28.5	9.9	19.0	3.6
Ti-G5	G5	152	3.2	6.9	0.1	6.8	1.5
Ti-R	rutile	-	3.0	3.5	1.3	2.2	0.6
Ti-NP	xerogel	150	2.9	26.7	16.9	10.1	3.0
Ti-KC	Krono clean7000	251*	3.2	27.9	16.0	11.9	3.6

[1]μmoles of NO and NOx eliminated and NO_2 produced under NO photooxidation reaction
[2]μmoles of NO_2 eliminated for NO_2 photocatalytic degradation ($NO_2 = 500$ ppb).
**data for sample at R.T.*

on the photocatalytic activity was analyzed from 0 to 80% RH. The concentrations of NO and NO_2 at the reactor inlet and outlet were measured using a NO, NO_2, NOx Chemiluminescence Thermo Environmental Instrument Inc. Analyzer. All the experiments were performed by following the steps detailed in the standard. Table 1 shows the main properties of the different TiO_2 samples under study and the photocatalytic activity results for NO and NO_2 photooxidation.

3 Results and Discussion

3.1 Characterization of the Samples

The TiO_2 commercial samples were characterized by different techniques. The main crystal phase detected for Ti-G5 and Ti-KC was TiO_2-anatase, meanwhile anatase and rutile are present on Ti-P25 and anatase, rutile, and a minor fraction of brookite are detected on Ti-NP [4]. These observations correspond to the band-gap energy obtained by UV–Vis spectroscopy (Table 1). Ti-KC was the material with higher specific surface areas, ranging between 250 $m^2\ g^{-1}$ for Ti-KC and ca. 50 $m^2\ g^{-1}$ for Ti-P25, see Table 1. Concerning the zeta potential measurement, Ti-NP and Ti-R showed isoelectric points (IEP) around pH 2, meanwhile the IEP shifts to higher pH values 5–6, for the others TiO_2.

3.2 NO Photooxidation Reaction

Figure 1 (left) shows the photocatalytic activity results of TiO_2 for the NO photooxidation reaction obtained with a photocatalyst loading of 3.0 mg cm^{-2}. The NO

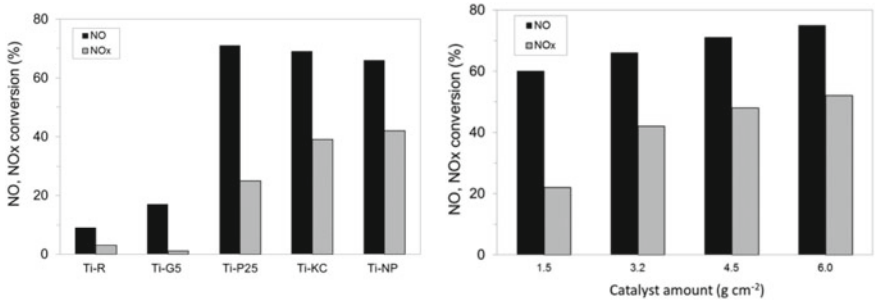

Fig. 1 NO and NOx conversion for TiO_2 based materials under ISO 22197-1:2007 standard. (left) Influence of the TiO_2 nature (TiO_2 loading = 3.0 mg cm^{-2}), (right) influence of the photocatalysts loading for Ti-NP

conversion goes below 20% to values around 70% for the most active materials. In all cases, NO_2 was observed as a reaction product, and then NOx conversion was calculated considering the eliminated NO and the produced NO_2. Maximum values were achieved for Ti-NP and Ti-KC, showing conversions near 40%. The NOx conversion trend was: Ti-NP ≈ Ti-KC > Ti-P25 > Ti-R > Ti-G5. In spite of the high surface area of Ti-G5, this material showed a low photocatalytic activity, and most of the NO was oxidized to NO_2 at the conditions of the ISO 22197-1:2007.

In order to assess the effect of the photocatalysts loading, the reaction was also conducted using photocatalysts loadings of 1.5 and 6.0 mg cm^{-2}. Figure 1 (right) shows the NO and NOx conversion values for Ti-NP. As it can be observed, the quantity of photocatalysts has an important influence in the total NOx elimination, decreasing the NO_2 released to the gas phase. Thus, a high photocatalysts loading allows reaching around 55% of NOx conversion. The same trend was observed for Ti-KC and Ti-P25. The obtained results with the reference material Ti-P25 are in line with previous works in the literature [6].

3.3 NO_2 Photooxidation Reaction

As NO_2 is one of the main pollutants found in urban areas, it is of great interest to study the performance of TiO_2-based materials for the NO_2 photooxidation reaction. The results obtained for 3.0 mg cm^{-2} TiO_2 loading and 500 ppb are reported in Fig. 2. As in the previous case, Ti-NP and Ti-KC show high photocatalytic activity. Moreover, it should be highlighted the photocatalytic performance of Ti-P25. NO_2 conversion near 50% was achieved for the most active TiO_2. This value could be higher for higher photocatalysts loading. FTIR analyses of samples before and after NO and NO_2 photooxidation reaction reveal the presence of nitrates species with a typical band center at 1384 cm^{-1}.

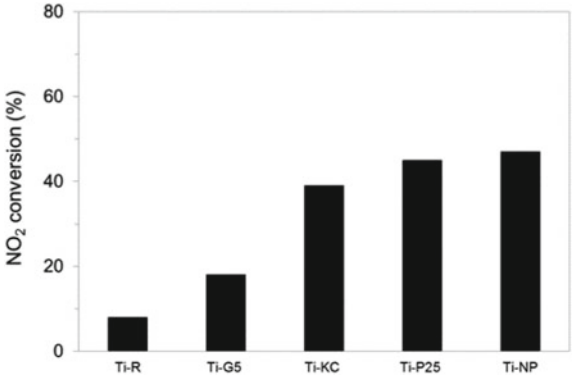

Fig. 2 Behavior of different TiO_2 based materials for the NO_2 photooxidation reaction under UV-A

The residence time is another important parameter that affects the photocatalytic performance. Thus, experiments at 0.5 to 1 s residence time were carried out. Doubling the residence time allows for a 10% increase of the NO_2 conversion. Moreover, the photocatalytic activity was maintained during the reaction time, indicating the stability of the materials at these operating conditions.

The effect of the relative humidity was studied for the most active TiO_2-based materials. NO_2 conversion declines with the increasing R.H. in all cases. This effect was more pronounced from 50% RH values. Finally, the behavior of the different semiconductors under low power visible light was analyzed and Ti-NP results the most active material with a NOx conversion near 12%.

4 Conclusion

The photocatalytic performance of different commercial and lab synthesized TiO_2 for the NO and NO_2 individual photooxidation reaction were studied. The photocatalyst loading has an important effect on the NOx elimination, reducing the NO_2 released into the gas phase. The results suggest that nitrates species were adsorbed on bulk TiO_2. NOx conversion values near 60% were attained for Ti-NP, Ti-P25 and Ti-KC. Regarding the NO_2 photooxidation reaction, conversion values near 50% were obtained for Ti-P25, Ti-KC, and Ti-NP. The TiO_2 synthesized through a sol technique showed the best photocatalytic performance under UV-A and Vis light. This result can be improved increasing the residence time and varying the relative humidity content.

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