

PHOTOCATALYTIC DESTRUCTION OF NO₂ AND HONO IN THE GAS PHASE USING TITANIUM DIOXIDE COATINGS

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ABSTRACT

An experimental set-up based on a diffusional technique was developed for studying the reactivity of photocatalytic surfaces. As an example of the usefulness of the method four commercially available building materials based on TiO₂ were investigated from the point of view of their reactivity towards NO₂ in absence and in presence of simulated tropospheric sunlight. Formation and removal of nitrous acid was also investigated. From measurements of NO₂ concentration, a reactivity coefficient and the corresponding deposition velocity were calculated. The method permits a fast and convenient way of assessing photocatalytic reactivity on a variety of surfaces.

INTRODUCTION

Nitrogen dioxide (NO₂) is a major pollutant which is produced by motor vehicles and other combustion processes. Nitrogen dioxide is harmful both for environment and human health due to the production of photochemical smog, acid deposition and peroxyacetyl nitrate (PAN). The removal of NO₂ using titanium dioxide (TiO₂) containing materials, provides a promising alternative to the more conventional methods for NO₂ emission control such as combustion modifications and dry and wet removal processes. TiO₂ is a semiconductor photocatalyst causing redox chemistry on the surface with ultraviolet photon radiation of wavelength less than 380 nm [1-3]. This light energy excites the electrons on the surface of titanium atoms moving them from the valence band to the conduction band. The result is the formation of electron-hole (e⁻-h⁺) pairs in the valence band. The produced electrons and holes can participate in various oxidation-reduction chemical reactions with suitable substances.

TiO₂ photocatalytic oxidation applied to nitrogen oxides has previously been reported [4-7]. Photocatalytic oxidation has also been applied to remove ambient NO₂ by coating TiO₂ on the walls of buildings and on paved roads [8]. NO₂ is converted to nitrates which can be easily washed away by rainfall. Although the utilization of TiO₂ has attracted a great interest, the actual factors controlling the photocatalytic activity of the catalyst are still unknown. The main purpose of this study is to develop a procedure for evaluating the photocatalytic destruction of gaseous pollutants on TiO₂ containing coatings. An application derived from the diffusion denuder technique, a well established analytical technique which is now widely used for air sampling [9-13], has been used.

EXPERIMENTAL

Figure 1 shows a schematic drawing of the apparatus used in the present study to collect the data reported. Cylindrical photocatalytic reactors coated with 4 different commercially available TiO₂ based products, were used in this investigation. The products were applied to the inside surface of the denuder via a wash coat technique. The diffusion denuder was positioned in a specially constructed cell opposite a quartz window which was illuminated via a 0.5 m flexible light guide, with UV-VIS radiation from a 150 W Xenon

lamp (Oriol, US). No filters were used to remove IR because the temperature rise during irradiation was negligible. Selected portions of the lamp output could be isolated with the use of appropriate filters. The radiant flux (in W/m^2) was measured by a radiometer whose head is settled in the place of the denuder.

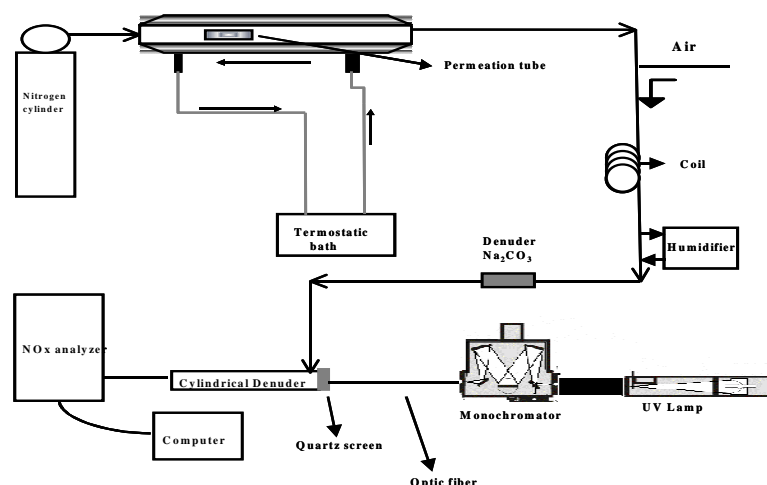


Fig. 1. Experimental set-up for evaluating of NO_2 photocatalytic destruction on TiO_2 coatings.

This provides a measurement of the incident irradiance reaching the walls in the same position as they are with regard to the source of light. In our experiments, the first three cm of the denuder walls were illuminated on average by 6.0 mW/cm^2 of UV light at 360 nm. The transition to the non-illuminated part of the denuder gradually occurs in the following 2-3 cm. The denuder was first conditioned by using the test atmosphere at controlled relative humidity (Humicon, DAS, Palombara S., Italy). The NO_2 concentration from a permeation tube was adjusted in a separate bypass circuit. An annular denuder coated with sodium carbonate was used to remove nitric and nitrous acids generated by heterogeneous reaction of NO_2 . The experiments were carried out as follows: first a flow of air at controlled relative humidity was admitted into the coated denuder to condition the surface. NO_2 was then added to the air flow and its outlet concentrations monitored by using a chemiluminescence analyser (API, Model 200A, US). After adsorption equilibrium was reached, the photocatalytic reaction was started by turning on the UV source. To check reproducibility all determinations were made in triplicate on the same coating.

RESULTS AND DISCUSSION

Diffusion denuders have developed into a well established analytical technique which is now widely used for air sampling when discrimination between gas phase and particulate matter is required [9-13]. In this study we used cylindrical denuders as photocatalytic reactors. By measuring the inlet and outlet concentration of NO_2 at a controlled relative humidity and in the presence or not of light, it has been possible to relate the decrease of concentration with the photocatalytic properties of the surfaces. Standard atmospheres containing NO_2 were

passed through cylindrical denuders, which were separately coated with materials A - D (Figures 2 and 3). Fig. 2a shows that in the case of material A rapid decrease in the NO_2 concentration was observed when the gas sample passed through each diffusion denuder. This surface reactivity showed a decrease over time. However, no change in the NO_2 concentration was obtained under UV illumination.

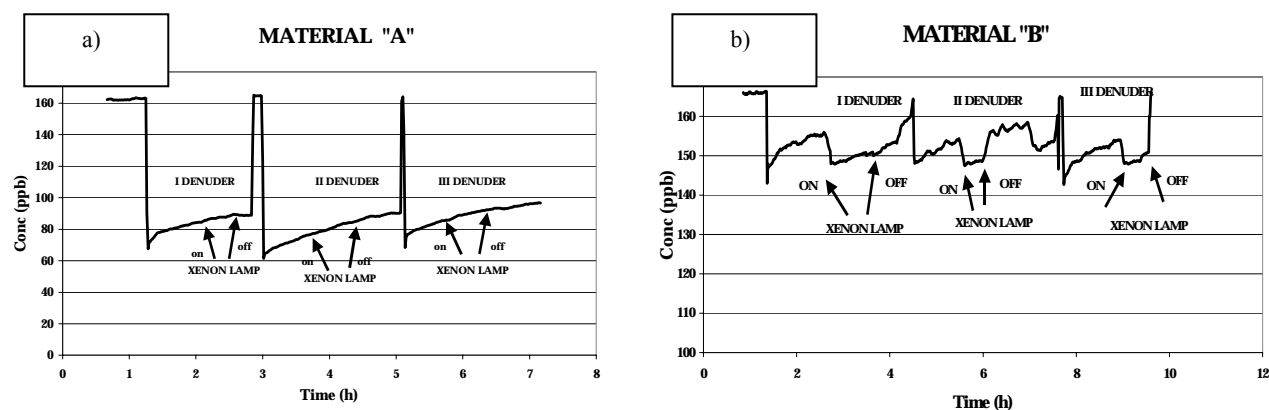


Fig. 2. Variation of NO_2 levels on cylindrical denuders coated with material A and B.

Figure 2b shows a lower reactivity of the material B as such in comparison to material A and a certain degree of photoactivity. Apparently, a decline in the photocatalytic reactivity takes place with prolonged reaction time.

Fig. 3a and 3b show that the material C revealed no type of reactivity whereas material D in contrast to all the other materials tested reveals a fairly high reactivity as such and a strong photoreactivity.

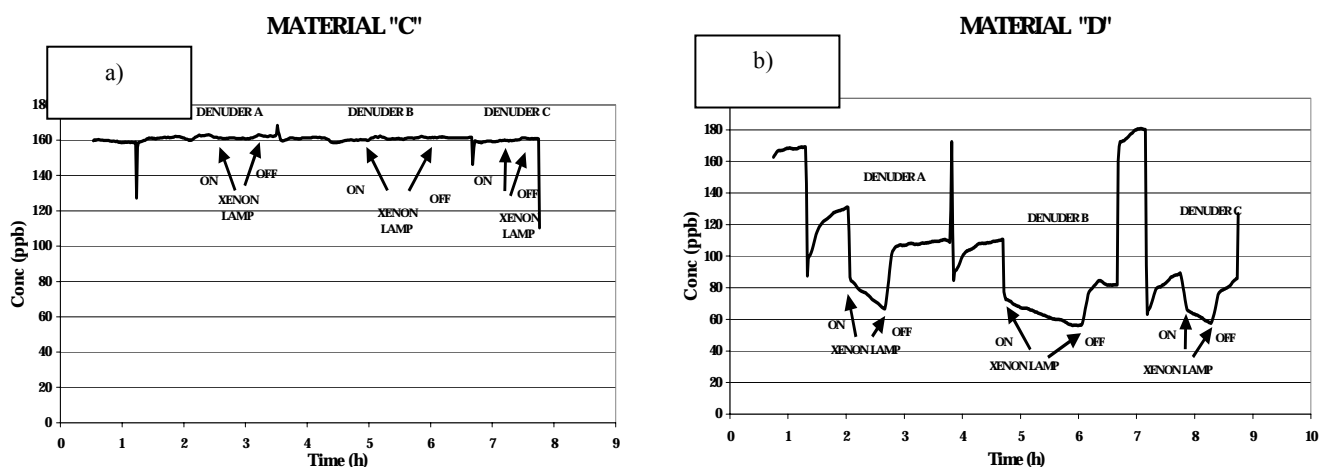


Fig. 3. Variation of NO_2 levels on cylindrical denuder coated with material C and D.

The potential conversion of NO_2 to HONO during the photocatalytic reaction has also been investigated. During the experiments, the NO_2 concentration in the effluent gas sample from the cylindrical coated denuder was measured with and without a diffusion denuder coated with sodium carbonate in order to collect nitrous acid. For all the materials

investigated here no change in the NO_2 concentration was observed demonstrating the absence of reaction products during the NO_2 photocatalytic destruction.

For comparison, a diffusion denuder was coated with a mixture of TiO_2 in water ($\text{TiO}_2/\text{H}_2\text{O} = 3/1$). Fig. 4 shows that UV illumination rapidly enhanced the reactivity of TiO_2 towards NO_2 collection.

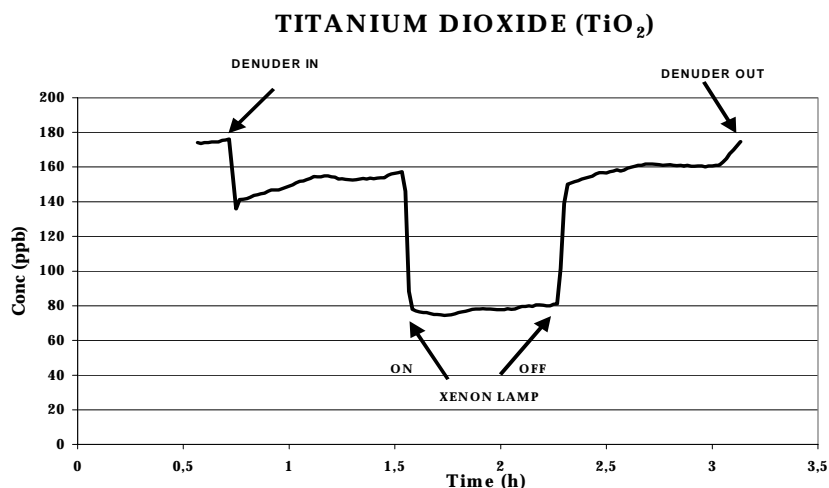


Fig. 4. Variation of NO_2 levels on cylindrical denuder coated with TiO_2 alone.

From Figures 2 and 3 it can be concluded that at the beginning of the experiment there is a drop in the concentration of NO_2 due to the reactivity of the surface in the case of materials A, B and D. When the light is turned on, there is a further increase in reactivity in the case of materials B and D. In general, as the photo reaction proceeds, less and less of the TiO_2 active surface is available as NO_2 is decomposed. Evidently, a decreased photocatalytic rate is to be expected with increased of illumination time. However, it is interesting to note that, in contrast to what can be observed for the surface “B”, the reactivity of surface “D” increases when the lamp is on. This result is at first sight counter-intuitive and not easy to interpret. At present the explanation of this behavior is unclear. One possibility is that the UV radiation plays a role in the photocatalytic process because of some reactions of chain transfer to generate more stable radicals that can diffuse within the reactive coating.

The data shown in figures 2-4 can be used for the evaluation of the reactivity of the materials under study. In heterogeneous catalytic reactions, mass transfer and surface reaction are two important factors controlling overall reaction rates. In general, the penetration efficiency E^j for a gaseous species j through a diffusion channel in laminar flow conditions depends on mass transfer to the walls. In fact, it is known that the rate limiting process for gas losses can be either due to diffusion or due to uptake at the surface, depending on the mass accommodation coefficient for the gas-surface collision. When the reaction rate on the surface is fast (i.e. the case with the coatings used for environmental sampling) the reaction along the channel is diffusion controlled. In these conditions, the collection efficiency follows the Gormley-Kennedy equation [14]. The use of diffusion denuders in studying the reactivity of photocatalytic surfaces results from the basic assumption that the surface reaction is the limiting step for mass transport to the walls. Under this condition uptake rates are independent of diffusion and a surface removal constant, dimensioned as a deposition velocity, containing

the accommodation coefficient as well as the rate constant for the surface reaction can be determined. When E^j is dependent on the surface reactivity, we have:

$$E^j = \frac{C(z)}{C_0} \cong \exp\left(-\frac{4Kz}{v_0 d_e}\right) \quad (1)$$

where C_0 is the mean concentration of the gaseous species j at the inlet of the channel, $C(z)$ is its concentration averaged over any cross-section located at a distance z from the axial coordinate origin, K is the surface reactivity constant, v_0 is the mean flow speed and d_e is the equivalent diameter of the channel, that is four times the ratio between the area and the perimeter (in our case the denuder diameter). Equation 1 has been utilized to analyze the data shown in the figures 2-4.

SURFACE	REACTIVITY CONSTANT (cm/s)		
	r.h. = 50%		
	K_s	K_p	K_{s+p}
Material A	0.0612	-	-
Material B	0.0076	0.0034	0.0094
Material C	0.0013	-	-
Material D	0.0471	0.0415	0.0835
TiO₂	0.0137	0.0620	0.0719

Table 1. The average values of reactivity constants and collection efficiencies for TiO₂ coatings

Each trial was conducted three times and average values were reported in the calculation in table 1. The average surface reactivity constant (K_s), photoreactivity constant (K_p) and the total reactivity constant (K_{s+p}) were also estimated for the four materials in comparison to TiO₂. The material D shows the highest K_{s+p} i.e. the best reactivity even in comparison to pure TiO₂. The materials A and C can be characterized in terms of K_s only with material A showing much larger reactivity compared to material C.

CONCLUSIONS

The features of the experimental set-up described in this paper can be summarised as follows:

- The system developed has been applied to study the photocatalytic properties of four commercially available materials on NO₂. A removal constant and therefore the deposition velocity for NO₂ in the presence or not of UV radiation has been calculated. A clear effect has been found on two surfaces (B and D) whereas on the surfaces A and C no effect induced by light was found. The surface A shows a rather high degree of reactivity as such. Surface C shows no reactivity at all.
- Since mass transport by diffusion has been expressly taken into account in the data analysis, the values measured would apply to the environment under

turbulent atmospheric conditions and represent the maximum rates of dry deposition

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