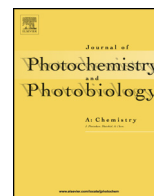




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Kinetics of the photocatalysed oxidation of NO in the ISO 22197 reactor



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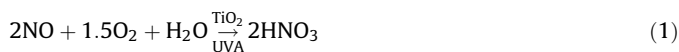
ABSTRACT

The photocatalytic reactor described in the NO_x removal ISO 22197-1:2007 is used to study the kinetics of the process, using a film of P25 TiO₂ which has either been conventionally pre-irradiated in a stream of air, or unconventionally in a stream of NO (1 ppmv). In the former case it is shown that the system does not achieve steady state exit levels of NO, probably due to the gradual accumulation of HNO₃ on the surface of the photocatalyst. The NO-preconditioned TiO₂ film demonstrated excellent steady-state levels when monitored as a function of NO concentration, [NO] and UV irradiance, ρ . However, in this case the photocatalytic reaction under study is NOT NO_x removal, but the conversion of NO to NO₂. It is shown that the kinetics of this steady state process fit very well to a kinetic expression based on a disrupted adsorption reaction mechanism, which has also been used by others to fit their observed (non-steady state) kinetics for NO_x removal on conventionally-(air) preconditioned films of P25. The appropriateness of this model for either system is questioned, since in both systems the kinetics appear to have a significant mass transport element. These findings suggest that mass transport and non-steady-state kinetics are likely to be significant features for most active photocatalytic samples, where the %NO conversion is >7%, and so limits the usefulness of the NO_x removal ISO 22197-1:2007.

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1. Introduction

The largest area of application for heterogeneous photocatalytic materials is as active coatings on architectural materials such as glass, tiles, concrete, paint and fabric [1–3]. In almost all cases, the photocatalyst is the non-toxic, UVA-absorbing semiconducting oxide, TiO₂. For many commercial photocatalytic products the key action of the coating is to remove NO_x, via its ability to mediate the photo-oxidation of NO_x by ambient oxygen to nitric acid [4–6]. In the case of the NO_x gas, nitric oxide, i.e. NO, the overall process can be summarised as follows [7]:



Although the end product is nitric acid, HNO₃, this less toxic, largely surface-bound species can then be washed away from the surface by rain. The photocatalysed oxidation of NO was considered of sufficient importance that it was the first granted ISO standard for photocatalysis, ISO 22197, published in 2007 [8]. Not surprisingly, the NO_x photo-reactor reported in that standard, the basic features of which are illustrated in Fig. 1, has attracted considerable attention, not least as a possible route to

understanding the observed kinetics of the photocatalysed Reaction (1) on different surfaces under varying conditions of NO concentration, [NO], and UV irradiance, ρ .

In a recent paper, Dillert et al. [9,10] reported on the kinetics of Reaction (1) using the above ISO 22197 photoreactor and a layer (2 mm thick) of P25 TiO₂ pressed onto a plexiglass rectangle (4.3 cm by 9.2 cm). Before use, these photocatalyst 'briquettes' were irradiated in air for 3 days with a UVA lamp, $\lambda_{\text{max}} = 355$ nm and $\rho = 1$ mW cm⁻², as a preconditioning step to remove all organic contaminants possibly adsorbed on the surface. Dillert et al. [9,10] then studied the kinetics of photocatalysis exhibited by these air-conditioned P25 briquettes as a function of both the incident UV irradiance, ρ , and average concentration of NO, [NO]_{av}, and fitted them to a 'disrupted adsorption' type photocatalyst rate expression [11], which has the following form:

$$r_{\text{NO}} = \chi_1(-1 + (1 + \chi_2\rho)^{0.5}) \frac{\chi_3[\text{NO}]_{\text{av}}}{(\chi_3[\text{NO}]_{\text{av}} + \chi_4 + \chi_1(-1 + (1 + \chi_2\rho)^{0.5}))} \quad (2)$$

where r_{NO} is the calculated rate, vide infra, and χ_1 – χ_4 are fitting constants that can be related back to processes within the reaction mechanism based on a disrupted Langmuir adsorption by the NO. Further details regarding this kinetic model can be found elsewhere [9–11]. In this kinetic model it is assumed that the observed kinetics are solely surface-controlled and comprise no

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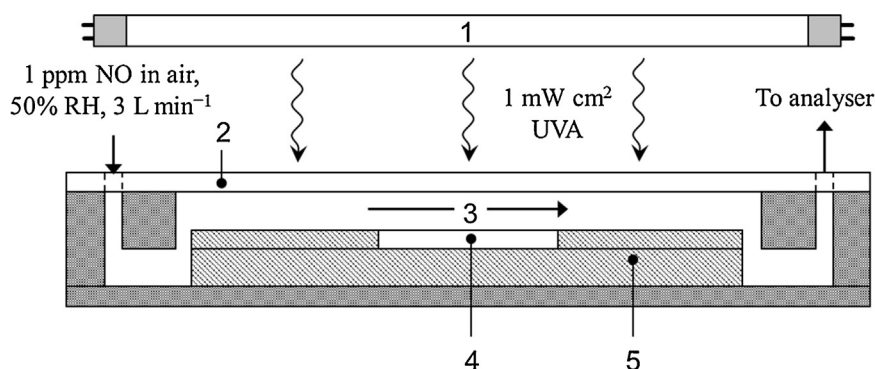


Fig. 1. Cross-sectional schematic of the photoreactor used in the NO air-purification ISO method: (1) UV light source, (2) glass cover, (3) test gas flow, (4) flat test sample, (5) height-adjusting plate.

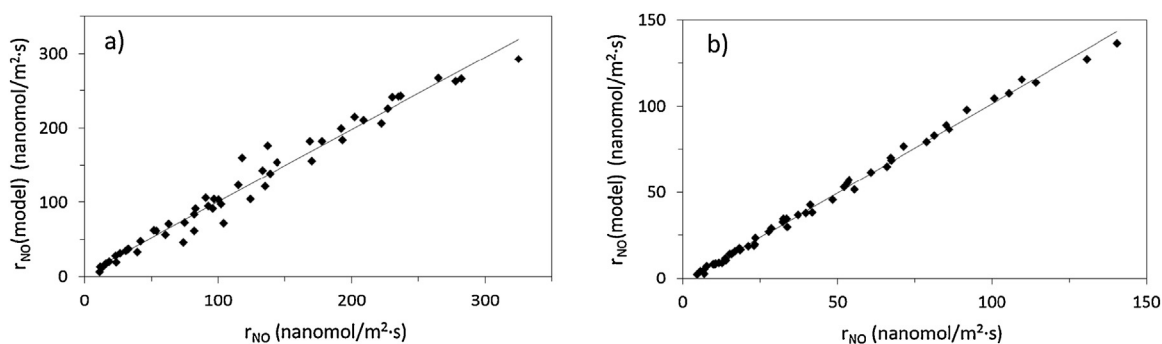


Fig. 2. Plots of the model calculated rate, $r_{\text{NO}}(\text{model})$, (calculated using Eq. (2) and the best fit constants given in Table 1) for each pair of ρ and $[\text{NO}]_{\text{av}}$ studied versus the measured rate, r_{NO} , for the same ρ and $[\text{NO}]_{\text{av}}$ pair, generated using a P25 film in an ISO NO_x reactor. The plots are for the kinetic data reported: (a) by Dillert et al. [9] for the photocatalysed Reaction (1), with $r^2 = 0.9730$ (for an air-preconditioned P25 film) and (b) here, for the photocatalysed Reaction (3) with $r^2 = 0.9954$ (for an NO-preconditioned P25 film), vide infra.

significant element of mass-transfer. The results obtained by Dillert et al. [9] are summarised in Fig. 2(a), which is a plot of the model calculated rate, $r_{\text{NO}}(\text{model})$, for each pair of ρ and $[\text{NO}]_{\text{av}}$ studied, found using a combination of the best fit constants listed in Table 1, and Eq. (2), versus the measured rate, r_{NO} , for the same ρ and $[\text{NO}]_{\text{av}}$ pair. This plot reveals what appears to be a reasonably good linear correlation between the calculated values of $r_{\text{NO}}(\text{model})$ and those determined experimentally, although the value of the correlation coefficient, r^2 , associated with this plot, 0.9730, see Table 1, is perhaps not too impressive and a reflection of the high degree of scatter in the plot in Fig. 2(a).

In a more recent paper [12], using the same photoreactor design and setup, we reported that, for P25 films, and several other different photocatalytic surfaces, the rate of Reaction (1) varies with irradiation time due to the accumulation of HNO_3 on the surface of the photocatalyst, i.e. on a pristine surface no steady-state rate is achieved for Reaction (1). Fig. 3a illustrates a typical set

of results for a film of P25 tested under ISO 22197 conditions and the photoreactor illustrated in Fig. 1. The results highlight the fact that the rate data reported by Dillert et al., and others [9,13–15], for this system are not for a photocatalytic system in the steady-state, as required by the kinetic model(s) used by these workers to fit their data. However, this problem is easily resolved, since we have found that pre-conditioning the photocatalytic film in NO, rather than air, creates a surface layer of HNO_3 , which leads to a truly steady-state rate for the photocatalysed oxidation of NO, as illustrated by the data in Fig. 3b for a NO-pre-treated P25 film. However, in this case the photocatalyst film is not mediating Reaction (1), but rather the conversion of NO to NO_2 , i.e.



This is not so surprising since Reaction (3) is known to be promoted by the presence of surface HNO_3 . Work with several different photocatalyst materials other than P25, such as a TiO_2 sol-gel film on glass and commercial photocatalytic paint and paper, has revealed that all are eventually rendered mediators of Reaction (3), rather than Reaction (1), when preconditioned for a sufficient period in a stream of NO so as to produce a steady-state surface concentration of HNO_3 . In this paper we report the kinetics of Reaction (3), as mediated by a NO-preconditioned film of P25 TiO_2 , as a function of ρ and $[\text{NO}]_{\text{av}}$ and explore the quality of fit to the observed kinetic data generated to Eq. (2), and consider the appropriateness of this kinetic expression as used here and by Dillert and others [9,13–16].

Table 1
Best fit values, based on Eq. (2), for the two reported data sets for the photocatalytic oxidation of NO.

Parameter	Units	Value	
		Dillert et al. [9]	This work
R^2		0.9730	0.9954
χ_1	$\text{mol m}^{-2} \text{s}^{-1}$	3.22×10^{-8}	1.51×10^{-9}
χ_2	$\text{m}^2 \text{s mol}^{-1}$	9.36×10^6	1.26×10^9
χ_3	m s^{-1}	2.44×10^{-2}	8.96×10^{-3}
χ_4	$\text{mol m}^{-2} \text{s}^{-1}$	4.95×10^{-7}	1.41×10^{-7}

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