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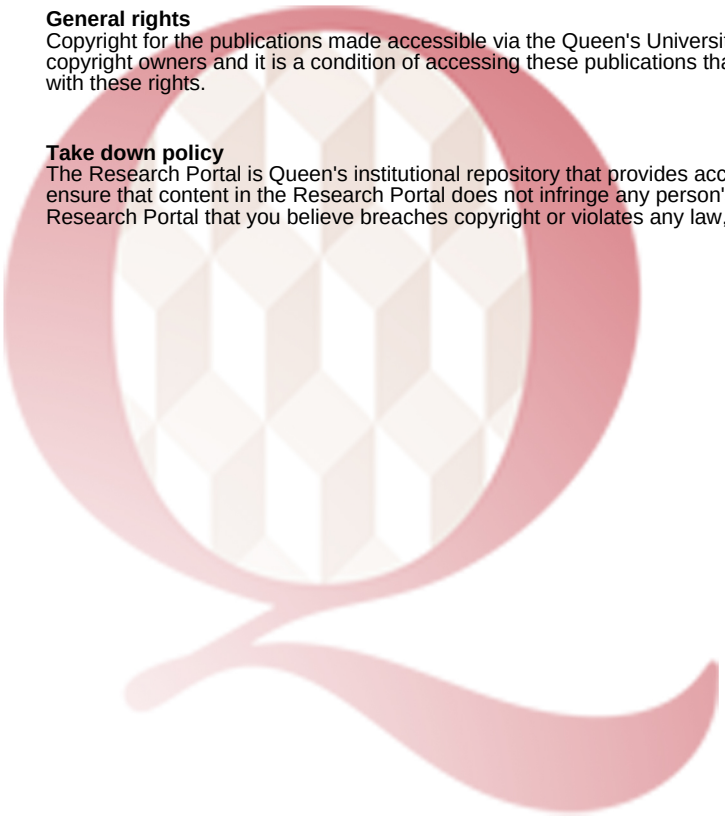

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Kinetics of the photocatalysed oxidation of NO in the ISO 22197 reactor

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Abstract

The photocatalytic reactor described in the NOx removal ISO 22197-1:2007 is used to study the kinetics of the process, using a film of P25 TiO_2 which has either been conventionally pre-irradiated in a stream of air, or unconventionally in a steam of NO (1 ppbv). 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 HNO_3 on the surface of the photocatalyst. The NO-preconditioned TiO_2 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 NOx removal, but the conversion of NO to NO_2. 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 NOx 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 NOx removal ISO 22197-1:2007.

Key words: Nitric oxide, NOx, ISO-22197, photocatalysis

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, TiO_2. 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]:

$$2NO + 1.5O_2 + H_2O \xrightarrow[UVA]{TiO_2} 2HNO_3 \quad (1)$$

Although the end product is nitric acid, HNO_3, 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 figure 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.

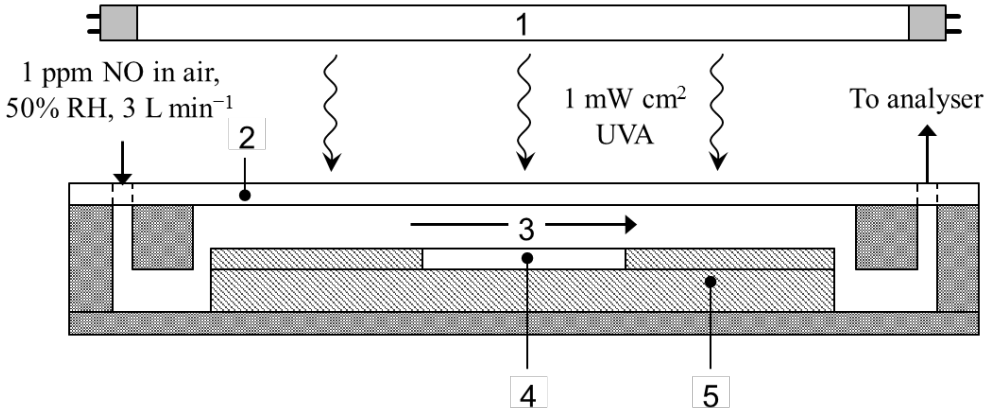

Fig. 1 Cross-sectional schematic of the photoreactor used in the NO air-purification ISO method: (1) UV light source, (2) glass cover, (3) test gas flow, (4) flat test sample, (5) height-adjusting plate.

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 TiO_2 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, λ_{max} = 355 nm and ρ = 1 mW cm^{-2}, as a preconditioning step to remove all organic contaminants possibly adsorbed on the surface. Dillert et al. 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:

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

where r_{NO} is the calculated rate, *vide infra*, and χ_1 to 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 significant element of mass-transfer. The results obtained by Dillert et al. [9] are summarised in figure 2(a), which is a plot of the model calculated rate, r_{NO}(model), for each pair of ρ and $[NO]_{av}$ studied, found using a combination of the best fit constants listed in table 1, and eqn (2), versus the measured rate, r_{NO}, for the same ρ and $[NO]_{av}$ pair. This plot reveals what appears to be a reasonably good linear correlation between the calculated values of r_{NO}(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 figure 2(a).

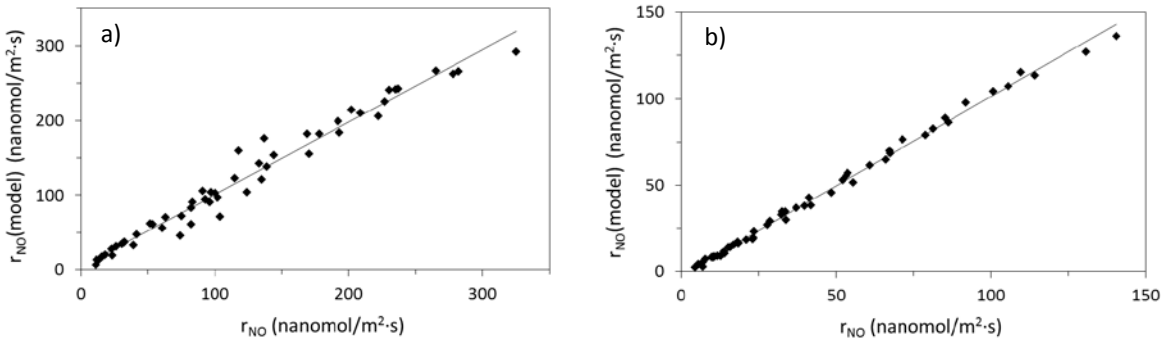

Fig. 2 Plots of the model calculated rate, r_{NO}(model), (calculated using eqn (2) and the best fit constants given in table 1) for each pair of ρ and $[NO]_{av}$ studied versus the measured rate, r_{NO}, for the same ρ and $[NO]_{av}$ pair, generated using a P25 film in an ISO NO_x reactor. The plots are for the kinetic data reported: (a) by Dillert et al. 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.

Table 1 – Best fit values, based on eqn (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	mol m^{-2} s^{-1}	3.22×10^{-8}	1.51×10^{-9}
χ_2	m^2 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	mol m^{-2} s^{-1}	4.95×10^{-7}	1.41×10^{-7}

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. no steady-state rate is achieved for reaction (1). Figure 3a illustrates a typical set of results for a film of P25 tested under ISO 22197 conditions and the photoreactor illustrated in figure 1. The results highlight the fact that the rate data reported by Dillert et al., and others [13-16], 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 figure 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.

$$2NO + O_2 \xrightarrow[UVA]{TiO_2,\ HNO_3} 2NO_2 \qquad (3)$$

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 $[NO]_{av}$ and explore the quality of fit to the observed kinetic data generated to eqn (2), and consider the appropriateness of this kinetic expression as used here and by Dillert and others.

1. Experimental

1.1. Materials

Unless stated otherwise, all materials were purchased from Aldrich Chemicals and used as received. The Degussa P25 TiO_2 powder is comprised of particles which are a mixture of mainly anatase and rutile phases (typically 70–80% anatase), and has a BET surface of ca. 50 $m^2\ g^{-1}$ [21]. Thin films of P25 were deposited on the glass substrates, 5 cm (width) × 10 cm (length) × 0.4 cm (thickness), by evaporation of 10 mL of a 2.5 g L^{-1} aqueous suspension of P25 spread evenly over the surface of the substrate (100 × 50 mm^2, 0.5 mg cm^{-1} loading) using a plastic syringe, at 300°C for 2 h in a muffle furnace. The dried films were found to be ca. 4 μm thick by SEM imaging.

1.2. Methods

The details of the ISO NO_x system used to test the NO_x removal capability of the different samples are reported elsewhere [12,14]. Briefly, the ISO NO_x standard employs an inert flat-bed photoreactor system, see figure 1, designed to hold a 5 cm (width = w) × 10 cm (length = L) test sample which can be irradiated with UVA light (ρ = 1 mW cm^{-2}). Humidified (RH = 50% at 25°C) air and dry NO, mixed to give an inlet NO concentration, $[NO]_{in}$, of 1.0 ppmv, are passed into the system at 3.0 L min^{-1}, which is regulated using mass flow rate controllers. The gas mixture is made to pass through a narrow gap (h) of 5 mm between the top glass window and the test sample below, and the outlet gas stream, with an outlet NO concentration, $[NO]_{out}$, from the reactor is sampled through a valve attached to a suitable NO_x detection system, usually based on chemiluminescence. In this work we used a Teledyne T200 chemiluminescence $NO/NO_2/NO_x$ analyser which took measurements every minute.

In the 2007 ISO NO_x standard it is recommended that the sample is preconditioned in air ($\rho \geq 1$ mW cm^{-2}, $t \geq 5$ h) [8]. Once (air) preconditioned, NO is introduced to the system and its concentration (and the concentration of NO_2) in the outlet stream is monitored for the ca. 30 min period before the light is switched on and during the 5 h irradiation period of the test, and for the 30 min period after the light has been switched off. As noted earlier, a typical set of data of [NO] vs time generated using this method and the P25 film used in this work is illustrated in figure 3(a). Although the decrease in the NO-removing capacity of the P25 film with increasing irradiation time is clear from the data illustrated in figure 3(a), it is a little less pronounced in the work of Dillert et al., who used an irradiation time of 2 h rather than the ISO stipulated value of 5 h. However, these workers also note that in their system 'no steady-state concentration of NO at the reactor outlet was reached' and as a consequence, for each kinetic run, in which the inlet [NO], $[NO]_{in}$, and ρ were varied, an average rate, r_{NO}, was calculated using the following expression:

$$r_{NO} = n(NO)_{rem}/(A.t_{(irrad)}) \qquad (4)$$

where A (= L × w) is the geometric area of the P25 film, $n(NO)_{rem}$ is the number of moles of NO removed ($\propto$ shaded area in figure 3(a)) and $t_{(irrad)}$ = irradiation time (= 7200 s in the work of Dillert et

al). The average concentration of NO, $[NO]_{av}$, used in the kinetic expression (2) was calculated using the following function:

$$[NO]_{av} = (1/2N)\Sigma([NO]_{in} + [NO]_{out,t}) \quad (5)$$

Where $[NO]_{out,t}$ is the outlet concentration at irradiation time t, and N is the total number of measurements of $[NO]_{out,t}$ made during an irradiation. Thus, in this work, for a 30 min irradiation, N = 30, since [NO] measurements were made every minute. Note: the expression used by Dillert et al. for calculating $[NO]_{av}$ is the same as that in eqn (5), except that they mistakenly suggest the difference rather than the sum of $[NO]_{in}$ and $[NO]_{out,t}$ should be calculated.

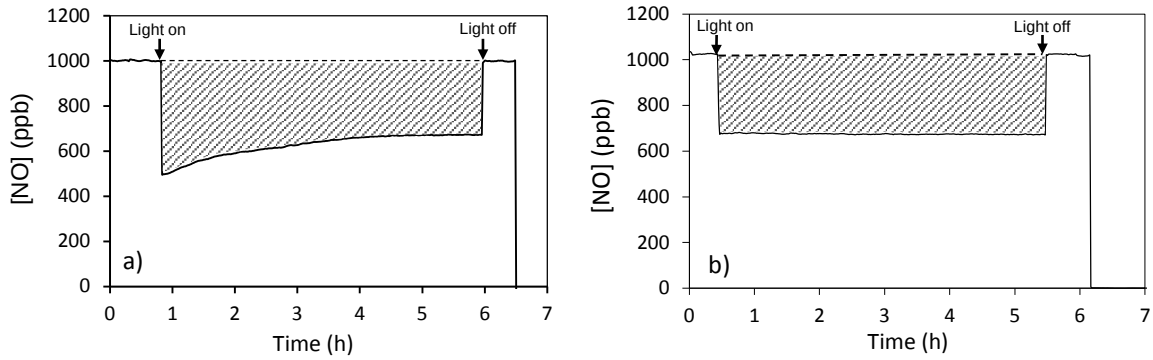

Fig. 3 Plots of NO concentration, [NO] (units: ppmv), vs time recorded using an ISO NO_x reactor under standard conditions (ρ = 1 mW cm^{-2}; flow (f) = 3 L min^{-1}) and a P25 film sample UVA preconditioned for 15 h at ρ = 1 mW cm^{-2} in a 3 L min^{-1} stream of (a) air and (b) air containing 1 ppmv NO. RH = 50%, T = 25°C.

In the work described here, the P25 film was, unless stated otherwise, always UVA preconditioned (1 mW cm^{-2}) in a stream of NO (1 ppm) for 5 h to produce a surface layer of HNO_3 that rendered the film an efficient photocatalytic converter of NO to NO_2, via reaction (3). When such films were used in the ISO reactor under otherwise standard conditions of flow rate, i.e. f = 3L min^{-1}, temperature (25°C) and relative humidity (RH = 50%), no evidence was found of significant (>5%) loss or drift in photocatalytic activity with regard to reaction (3) with irradiation time, as illustrated by the results in figure 3(b). It was this NO-preconditioned P25 film that was used to carry out a study of the kinetics of reaction (3) as a function of ρ and $[NO]_{av}$, using the otherwise standard ISO conditions of f, T and RH described above.

2. Results and Discussion

The results illustrated in figure 3(b) reveal that a NO-preconditioned film exhibits no obvious sign of drift (<5%) under steady-state illumination with UVA over the whole time-course of the 5 h irradiation period. Given this stability, and in order to speed up the time taken to conduct the study of the kinetics of reaction (3), in a typical run the irradiance was set at a known value of ρ within the range 0.01–2 mW cm^{-2}, and the inlet level of NO, $[NO]_{in}$, was then systematically varied in a step-wise fashion over the range 0.05–1.00 ppm. At each $[NO]_{in}$, the 30 min irradiation period was preceded and proceeded by a 15 min dark equilibration period. A typical set of results arising from this work, generated using an irradiance of 1 mW cm^{-2}, is illustrated in figure 4. For each different $[NO]_{in}$ value, the amount of NO removed, $n(NO)_{rem}$, (proportional to the corresponding hatched area in figure 4) was calculated and found to be the same as the amount of NO_2 generated, confirming

that this system is a study of reaction (3) on a NO-preconditioned P25 film. Each measured value of $n(NO)_{rem}$ was used to calculate a specific value for the rate of reaction (3), r_{NO}, using eqn (4), for the fixed, known value of ρ (1 mW cm^{-2} in figure 4) with A = 50 cm^2 and $t_{(irrad)}$ = 1800 s. This rate was then paired with the associated average concentration of NO used, $[NO]_{av}$, which was calculated using equation (5). Thus, each of the hatched areas illustrated in figure 4 generated a r_{NO}, $[NO]_{av}$ pair for the set ρ value used, in this case ρ = 1 mW cm^{-2}. The irradiance was then altered to another fixed and known value, say 0.8 mW cm^{-2}, and another profile similar to that illustrated in figure 4 was generated to yield another collection of r_{NO} vs $[NO]_{av}$ data, but this time for ρ = 0.8, rather than 1 mW cm^{-2}. This process was repeated until the whole irradiance range of 0.01 to 2 mW cm^{-2} had been covered.

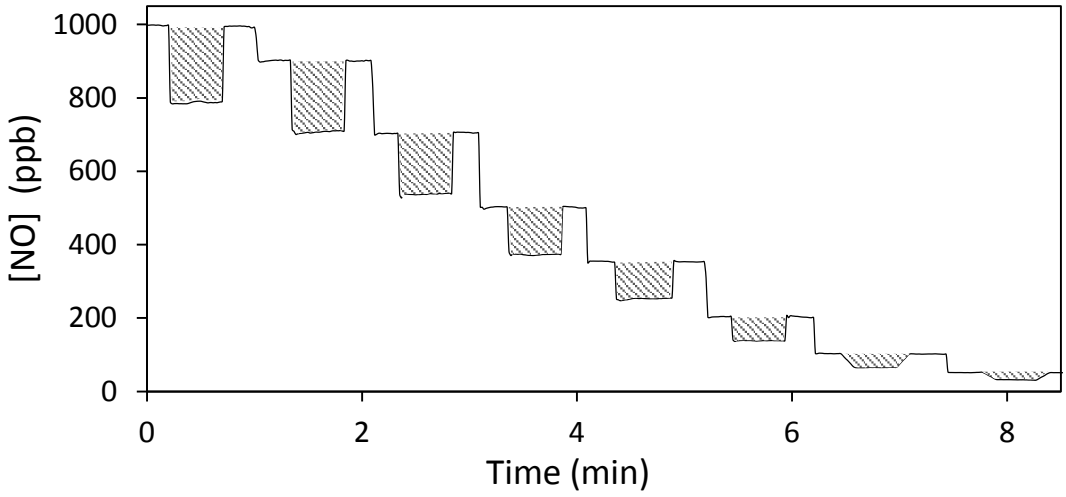

Fig. 4 Plot of NO concentration, [NO] (units: ppbv), vs time recorded for the ISO NO_x reactor for a NO-pre-treated P25 covered sample under otherwise standard conditions (ρ = 1 mW cm^{-2}; flow (f) = 3L min^{-1}, RH = 50%, T = 25°C). The inlet level of NO, $[NO]_{in}$, was systematically varied 8 times from 1000 to 50 ppbv. The shaded areas ($\propto n(NO)_{rem}$) highlight the change in [NO] upon illumination for 30 min, between 15 min-long dark (equilibration) periods. For each illumination, the average value of NO in the reactor during the illumination, $[NO]_{av}$, see eqn (5), and the amount of NO removed (and converted to NO_2), n_{rem}, were determined and used to calculate the average rate of NO removal, r_{NO}, using eqn (4). The obtained values of r_{NO} were then best-fitted to the rate expression, eqn (2), using the known values of $[NO]_{av}$ and ρ.

A 3D plot of the rate data obtained from this systematic study of r_{NO} as a function of $[NO]_{av}$ and ρ, with r_{NO} as the z-axis and ρ and $[NO]_{av}$ as the x and y axes, respectively, is illustrated in figure 5. In this diagram, the lines of best fit were generated using eqn (2) and the optimum fit to the data parameters given in table 1. Figure 2(b) illustrates an alternative plot of this data, as favoured by Dillert et al., i.e. a plot of the calculated rate, r_{NO}(model), for each pair of ρ and $[NO]_{av}$ studied, determined using eqn (2) and the best fit constants in table 1, versus the actual measured rate, r_{NO}, for the same ρ and $[NO]_{av}$ pair. A quick comparison of the latter plot of the data reported here for reaction (3), with its high value of r^2 (0.9954) for the NO-preconditioned data, with that generated by Dillert et al. for their air-conditioned P25 film (r^2 = 0.9730), for reaction (1), clearly shows that a

NO-pre-conditioned P25 film generates kinetic data for reaction (3) which is a better fit to the rate expression, eqn (2), than the kinetic data by reported by Dillert et al. for the photocatalysed promotion of reaction (1) by an air-conditioned P25 film. This is perhaps not too surprising given that, in contrast to the current study, in the work by Dillert et al. the necessary condition of achieving steady state levels of NO under illumination was not achieved, as noted earlier and illustrated by the data in figure 3(a), whereas clearly, from the data in figures 3(b) and 4, the necessary steady-state kinetics were achieved for the NO-pretreated P25 film.

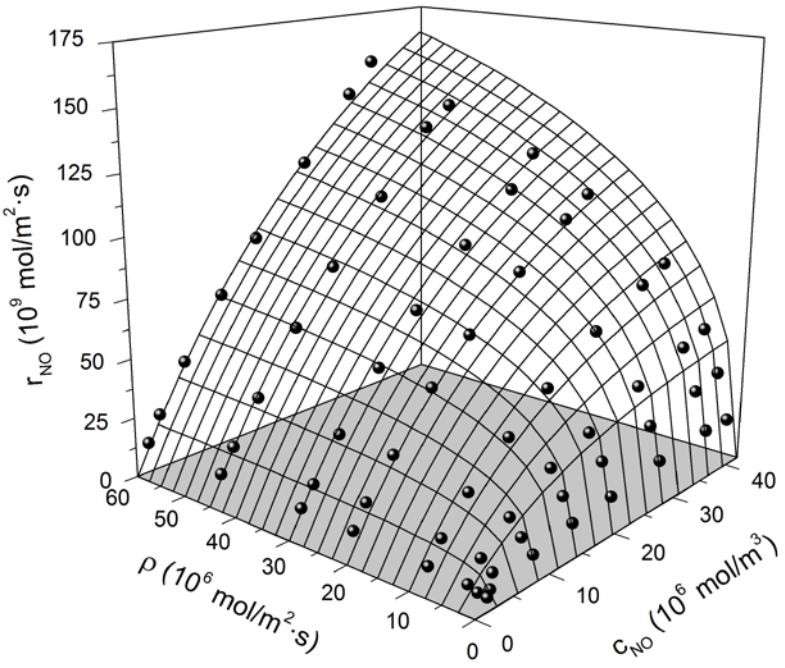

Fig. 5 3D plot of the rate data obtained from the present systematic study of r_{NO}, for reaction (3), as a function of $[NO]_{av}$ and ρ, with r_{NO} as the z-axis and ρ and $[NO]_{av}$ as the x and y axes.

2.1. Is the kinetic model appropriate?

It is useful at this stage to remember that even if a kinetic dataset does provide a good fit to a kinetic model generated rate expression, such as eqn (2), it does not necessarily mean that that model is appropriate. Thus, unfortunately, in the system studied here it can be clearly and simply shown that although the fit to the kinetic data is attractively good, the kinetic model itself is not appropriate. Simply put, the kinetic model used to generate eqn (2) is inappropriate here and elsewhere when applied to the photocatalytic oxidation of NO, since it makes the basic – and demonstrably incorrect – assumption of no significant dependence of the observed kinetics on the mass transport of NO to the photocatalytic film.

Hunger et al. [13-16] have modelled the kinetics of an ISO photocatalytic type reactor for the removal of NO in which mass-transport is the limiting step, and derived the following key expression that relates the outlet level of NO, $[NO]_{out}$ to the inlet level of NO, $[NO]_{in}$, and the reactor volume, V (25 cm^3), height, h (0.5 cm), and flow rate, f (3 L min^{-1} ≡ 50 cm^3 s^{-1}):

$$C_{out}/C_{in} = (100 - \%\text{conversion})/100 = \exp(-Sh.D.V/(2h^2f)) \qquad (6)$$

Where Sh is the Sherwood number, i.e. the ratio of convective to diffusive mass transport in the reactor, and D is the diffusion coefficient for NO (ca. 0.171 $cm^2\ s^{-1}$). The value for Sh used here, 6.85, was calculated using the expression:

$$Sh = 0.66Re^{0.5}Sc^{1/3} \quad (7)$$

Where Re and Sc are the Reynolds and Schmidt numbers for the system. The Reynolds number used here (= 120) was calculated using:

$$Re = v.d_h/\upsilon \quad (8)$$

Where v is the gas velocity (20 cm s^{-1} for a flow rate of 3 L min^{-1}), d_h is the hydraulic diameter (0.91 cm for the ISO reactor) and υ is the kinematic viscosity (0.151 $cm^2\ s^{-1}$ for air). The Schmidt number used here (= 0.883) was calculated from the ratio υ/D.

It follows from eqn (6), and the values of Sh, D, V and h, that if the photocatalysed removal of NO is purely mass-transport-controlled in the ISO reactor, at f = 3 L min^{-1} (50 $cm^3\ s^{-1}$), the expected %conversion would be ca. 70%, **regardless of the value of $[NO]_{in}$**. It also follows that for the kinetics **not** to have any significant contribution due to mass transport, it is necessary that the measured %conversion (at 3 L min^{-1}) should be much smaller than 70%, say <7.0%, i.e. at least <10% of the maximum value achievable. Figure 6 is a plot of the measured %conversion as a function of the relative irradiance, ρ/ρ_o, where ρ_o = 2 mW cm^{-2}, for all the different values of $[NO]_{in}$ tested in this work. The top broken horizontal line illustrates the estimated maximum %conversion (70%) that could be achieved if the photocatalysed removal of NO was solely mass-transport controlled. From this plot of the measured values of %conversion as a function of $[NO]_{av}$ and ρ/ρ_o, it is clear that in most cases the %conversion observed is >> the 7.0% upper limit (the lower broken line) described above that might be considered appropriate if mass transport made no significant contribution to the kinetics. As a consequence, it appears that most of the rate data generated in this work will have a significant mass-transport component. In addition, from this same plot it is clear that the contribution of mass-transport to the overall observed kinetics increases with decreasing $[NO]_{in}$ and increasing ρ/ρ_o values, as would be expected. The data in figure 6 strongly suggest that it is inappropriate to fit the rate expression given in eqn (2) to the kinetics reported here, as the rate expression is derived from a kinetic model that assumes no mass transport control. The kinetic data reported by Dillert et al., for reaction (1), photocatalysed by a briquette of P25, were analysed similarly and a selection of the results are illustrated in Figure 7. Not surprisingly, these results exhibit the same high conversion under most conditions of [NO] and ρ as the data in figure 6, implying that the data suffers the same problem as reported above, i.e. in most cases there is a significant (>10%) mass-transport contribution to the reported rates. It follows, therefore, that the rate equation, eqn (2), used by Dillert et al., to interpret their kinetics, is also not appropriate.

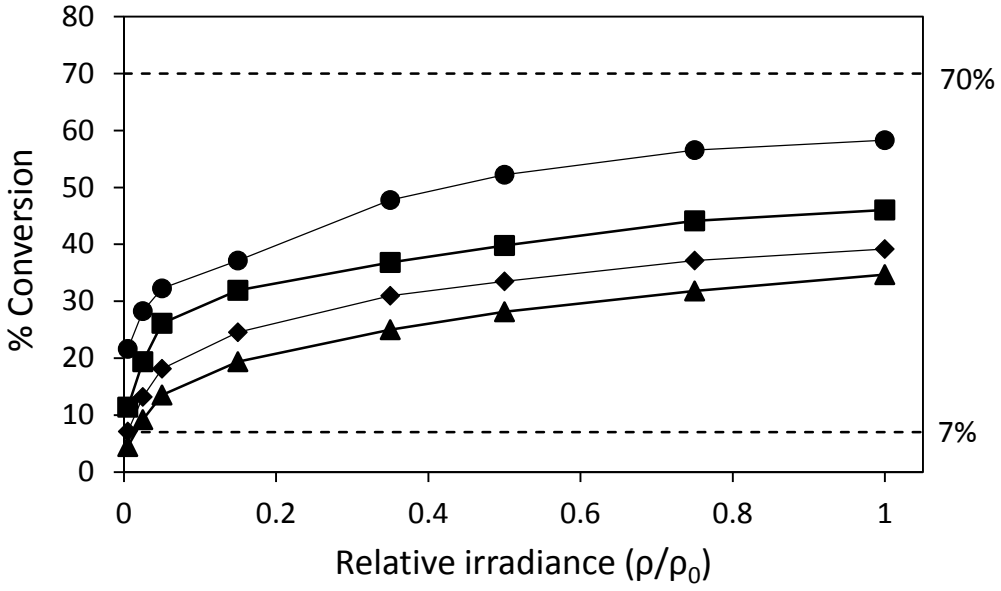

Fig. 6 Measured %conversion (of NO) as a function of relative irradiance, ρ/ρ_o, for some of the $[NO]_{in}$ levels used in this work with a NO-preconditioned P25 film ($[NO]_{in}$: 50 (●), 200 (■), 500 (◆) and 1000 (▲) ppb). The two broken lines represent the maximum conversion possible (based on mass transport control), 70%, and 10% of this value, i.e. 7% conversion, that represents a minimum value below which the kinetics are largely activation controlled.

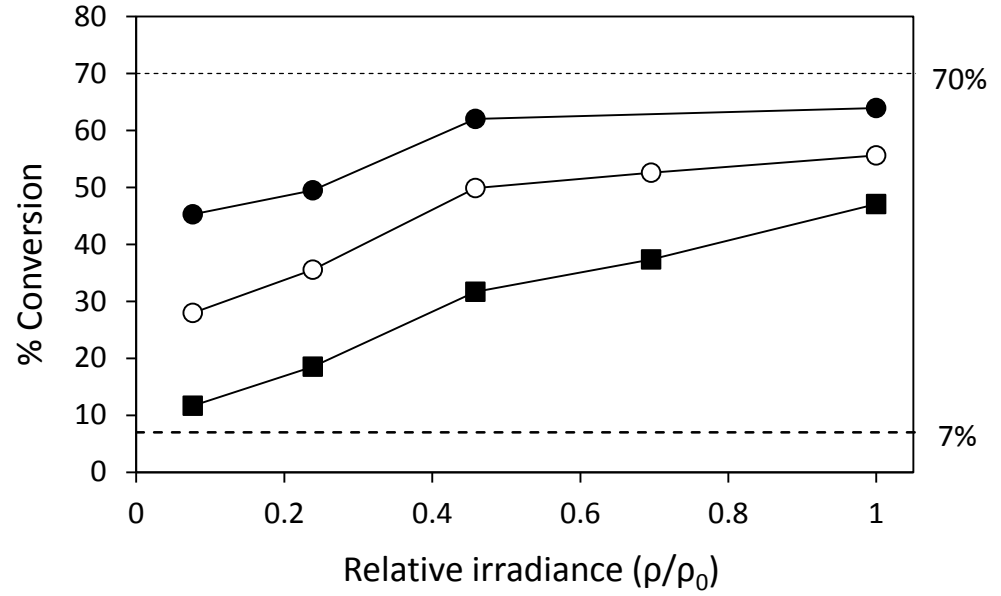

Fig. 7 Measured %conversion (of NO) as a function of relative irradiance, ρ/ρ_o, for some of the $[NO]_{in}$ levels used in the work of Dillert et al. with an air-preconditioned P25 film ($[NO]_{in}$: 49 (●), 415 (○) and 1297 (■) ppb). The two broken lines represent the maximum conversion possible (based on mass transport control), 70%, and 10% of this value, i.e. 7% conversion, that represents a minimum value below which the kinetics are largely activation controlled.

It can be shown that, for purely mass transport controlled kinetics for the removal of NO in the ISO NO_x reactor at 25 °C, eqn (6) can be re-written as:

$$C_{out}/C_{in} = \exp(-(0.66Sc^{1/3}.D.V.d_h^{0.5})/(2h^2(f.\upsilon.h.w)^{0.5})) = \exp(-8.4/f^{0.5}) \quad (9)$$

since the Reynolds number depends directly upon f. Thus, it should be possible to gather evidence for mass-transport controlled kinetics for reaction (3) by determining the fraction of NO converted (to nitric acid), i.e. C_{out}/C_{out}, for a series of different low flow rates, in this case spanning the range: 0.5 to 1.5 L min^{-1}, under conditions which would further favour mass-transport controlled kinetics, i.e. low $[NO]_{in}$ (50 ppb) and high irradiance, ρ (2 mW cm^{-2}). A plot of the data so obtained in the form of $\ln(C_{out}/C_{in})$ vs $1/f^{0.5}$ is illustrated in figure 8, and reveals a reasonable linear relationship, especially at the lowest flow rates, where mass-transport control would be favoured. The gradient of the line of best fit to the data is 9.3 s cm^{-3}, which is not far from that predicted by theory, 8.4 s cm^{-3}.

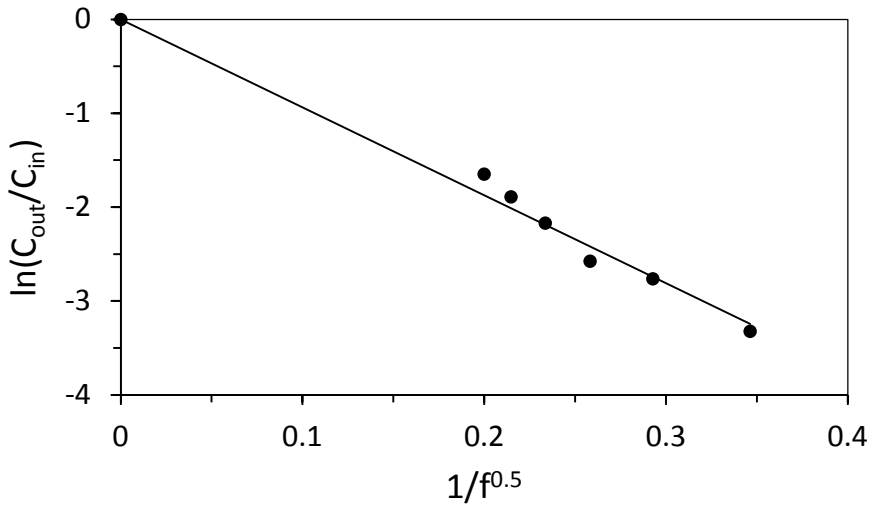

Fig. 8 Natural logarithm of fraction of NO converted against $1/f^{0.5}$ with a NO-preconditioned P25 film at low $[NO]_{in}$ (50 ppb) and high irradiance, ρ, (2 mW cm^{-2}) for low flow rates of 0.5 to 1.5 L min^{-1}; r^2 = 0.9858

Conclusions

The current ISO NO_x test yields kinetic data for P25 films, and many other high-activity materials, including commercial photocatalytic paints and sol-gel films, that have a significant mass-transport component and do not usually exhibit steady-state kinetics. A high activity material is defined here as one that yields a %NO removal value of >7% under standard NO_x ISO conditions. UVA preconditioning of such films in a stream of NO improves the steady-state nature of the kinetics, but alters the process from reaction (1) – a NO_x lowering reaction and the essence of the ISO NO_x test – to reaction (3), the antithesis of the ISO test as it produces no change in NO_x-level, since it probes the ability of the photocatalyst to effect the oxidation of NO to NO_2, reaction (3). However, such pre-treated P25 films also exhibit high %conversion values under most values of $[NO]_{in}$ and ρ studied, and so too will have a significant mass transport component to their kinetics.

A significant component of mass transport control represents a clear general problem with the ISO NO_x test as it currently stands, and so the test, for NO_x removal capability, needs to be modified so that this feature is at least acknowledged if not addressed. For example, it needs to be stated that when using the ISO NO_x test under standard conditions (i.e. f = 3 L min^{-1}), an accurate measure of photocatalytic surface activity, rather than a mixture of surface- and mass-transport kinetics, of the sample under test will only be gained if the sample exhibits a %conversion value that is <7%. In addition, it needs to stated that for measured %conversion values >7% the kinetics will become increasingly mass-transport controlled the higher the %conversion measured, **and** that the highest %conversion value (where the kinetics are purely mass-transport controlled) which can be expected (at f = 3 L min^{-1}) will be ca. 70%.

It is suggested here that a more useful probe of gas-phase **photocatalytic** activity would be a modified version of the ISO NO_x test in which the UV irradiance is <<1 mW cm^{-2}, so as to ensure the measured %conversion is <7%. However, as noted earlier, most samples do **not** generate steady-state concentrations of NO under illumination, due to the accumulation of a surface layer of HNO_3, which alters the kinetics of NO removal. Thus, it is also suggested that the modified ISO NO_x test should require that the samples be pre-conditioned under a stream of NO (1 ppm), with ρ = 1 mW cm^{-2}, to ensure the creation of a uniform layer of HNO_3 so that that the photocatalytic reaction under test is reaction (3), i.e. the photocatalysed oxidation of NO to NO_2, and that steady-state levels of NO and NO_2 are generated. Obviously, if these changes were adopted, such a modified test should not be called a NO_x test, but rather a test of gas-phase photocatalytic activity, for reaction (3), which can also yield useful mechanistic information, through an examination of %conversion as a function of $[NO]_{in}$ and ρ. Work is currently in progress on such a modified test, and the results will be reported later. As it stands, the current ISO NO_x test does not yield data that can be readily and directly related to photocatalytic activity for any sample which exhibits a %conversion value (at f = 3 L min^{-1}) >7%, and this represents a serious drawback to the test.

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