Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
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Light intensity dependence of the kinetics of the photocatalytic oxidation of nitrogen(II) oxide at the surface of TiO_2

Supporting Information

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I.

The photocatalytic oxidation of NO was accomplished according to ISO 22197-1 [20], employing a set-up (Figure S-1) consisting of an air and a test gas supply, three mass flow controllers ①, a humidifier ②, a static mixer ③, a four-way valve ④, a photoreactor (PMMA, borosilicate glass) containing the sample ⑤, a light source ⑥, and a chemiluminescent NO-NOx analyser ⑦.

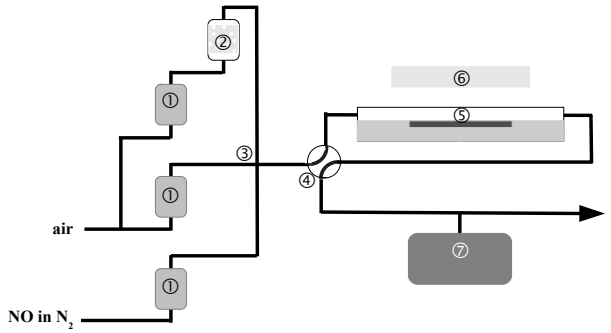

Figure S-1: Scheme of the experimental set-up.

At the beginning of each individual test run the NO volume concentration was adjusted within a range from 0.05 to 1.3 ppm ($c_{NO,in}$ = (2 – 53)·10^{-6} mol m^{-3}) via a bypass mode without photoirradiation. Therefore, a flow of the carrier gas (usually oil-free air, in some experiments N_2, and O_2) of 3.0 L min^{-1} was combined in a mixing chamber with the needed NO flow ((3.0·– 80)·10^{-3} L min^{-1}; 50 ppm NO in N_2, Linde). Having established the constant volume concentration a dark adsorption of the pollutant on the catalyst surface was accomplished by switching from bypass into reactor mode. After the pollutant volume concentration had risen up to the initial NO concentration again the photoirradiation (E = 0 – 15 W m^{-2} = 0 – 44.8·10^{-6} mol photons m^{-2} s^{-1} with λ_{max} = 365 nm)) was performed for 2 h. At the end of the degradation reaction the lamp and the NO-flow were switched off simultaneously. The NO concentration was continuously monitored until it had decreased to 0 ppm.

II.

A Langmuir-Hinshelwood-type rate law (eq. 19) comprising of four kinetic parameters was derived

$$ {}^{r}r_{NO} = \chi_1\left(-1+\sqrt{1+\chi_2 E}\right)\frac{\frac{{}^{a}k_{NO}}{1+K_{H_2O}c_{H_2O}}c_{NO}}{\frac{{}^{a}k_{NO}}{1+K_{H_2O}c_{H_2O}}c_{NO}+{}^{d}k_{NO}+\chi_1\left(-1+\sqrt{1+\chi_2 E}\right)} \qquad (19) $$

to describe the influence of the pollutant concentration and the photon flux on the rate of the photocatalytic oxidation of nitrogen(II) oxide. The exact determination of the four kinetic parameters is crucial to this study since the values of χ_1, and χ_2 decide if there is a linear or square root dependence between the reaction rate ${}^{r}r_{NO}$ and the light intensity E.

To determine the four parameters χ_1, χ_2, ${}^{a}k_{NO}/(1+K_{H_2O}c_{H_2O})$ and ${}^{d}k_{NO}$ the sum of the squared errors

$$ SSE\left(\chi_1,\chi_2,\frac{{}^{a}k_{NO}}{1+K_{H_2O}c_{H_2O}},{}^{d}k_{NO}\right) = \sum_{i=1}^{n}\left(r_{NO,i}^{calc}\left(\chi_1,\chi_2,\frac{{}^{a}k_{NO}}{1+K_{H_2O}c_{H_2O}},{}^{d}k_{NO},E_i,\bar{c}_{NO,i}\right)-r_{NO,i}^{meas}\right)^2 \qquad (S\text{-}1) $$

(= objective function) was used as the optimization criterion with $r_{NO,i}^{meas}$, and $r_{NO,i}^{calc}\left(\chi_1,\chi_2,\frac{{}^{a}k_{NO}}{1+K_{H_2O}c_{H_2O}},{}^{d}k_{NO},E_i,\bar{c}_{NO,i}\right)$ being the experimentally determined reaction rates, and the rates calculated using equation 19, respectively.

In a first attempt the excel solver was used to solve this optimization problem. Since it is a gradient based local optimization algorithm whose outcome is highly dependent on the initial guess of parameters no consistent solution was obtained. It can be assumed that the objective function *SSE* has many local minima and/or sharp edges and discontinuities. So it is inevitable to use a global optimization technique like a genetic algorithm (GA) or a particle swarm optimization (PSO) to receive optimal or near-optimal parameter values.

Genetic algorithm (GA)

Implementation details of the GA can be found in reference [S1], therefore, only a brief overview over the optimization procedure is given here. The sequence of steps used in the GA is summarized in Figure S-2.

The first step of the optimization procedure is the generation of an initial population consisting of a given number of random individuals. Each individual is a vector containing the four parameters of the kinetic model (eq. 19) with each one set to a random value taken from a predetermined interval that limits the search space. Then, for each individual, the objective function is evaluated: the parameters are substituted into the model and then the *SSE* between the model prediction and the experimental data is calculated. Depending on these errors, in the GA terminology called fitness, the individuals are further processed by calculations mimicking the biological concept of evolution (selection, recombination with crossover, and random mutation). As selection method the roulette wheel selection was used: Each individual is chosen as a candidate for the recombination step with a probability proportional to it's fitness. During crossover the individuals are paired together and with a certain probability (Xover chance) two values of the kinetic parameters (genes) are exchanged between them. This is done for all pairs and all genes but the first. Finally during the

mutation step one value of the four kinetic parameters of an individual is changed to a random value with a given probability (mutation rate). These steps are not applied to all individuals to make sure that no near-optimal solutions are lost due to random effects like mutation. Therefore, a subset of individuals, which size is controlled by a parameter called generation gap, is directly transferred to the next generation. The result from these steps is a new generation of the same number of individuals. Then the process is repeated with the new generation as starting point. Over many generations those individuals that lead to small *SSE* become dominant in the population. A fixed maximum generation number is used as stopping criterion. The individual with the lowest error of the last generation is then used as input to a simplex algorithm to ensure a local (or even the global) minimum is reached.

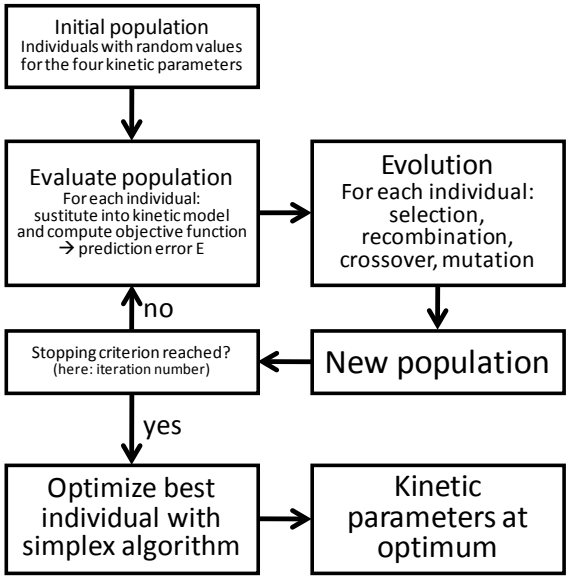

Figure S-2: Scheme of the parameter optimization with a genetic algorithm (GA).

Table S-1: Intervals for the parameters of Eq. 19 limiting the search space.

Parameter	Minimum	Maximum
χ_1	10^{-9}	10^{9}
χ_2	10^{-9}	10^{9}
${}^{a}k_{NO}/(1+K_{H_2O}c_{H_2O})$	10^{-9}	1
${}^{d}k_{NO}$	10^{-9}	1

During creation of the initial population random values from four intervals, one for each kinetic parameter, are assigned to the individuals. These intervals are also taken into account during the mutation and crossover steps, so individuals with values outside the solution search space defined by these intervals can never occur. The limits have to be chosen to ensure that solutions without a chemico-physical meaning, e.g. values ≤ 0, are expelled. Moreover the solution search space has to be wide enough to find the global optimum.

In this work the GA was programmed in C#.Net. The intervals for the four kinetic parameters of Equation 19 defining the search space for the minimal value of the *SSE* are given in Table S-1. The values of the constants controlling the GA (number of individuals, maximum number of generations, mutation rate, Xover chance, and generation gap) are given in Table S-2.

Table S-2: Constants to control the GA.

Parameter	Value
Number of individuals	10^{6}
Maximum number of generations	10^{3}
Mutation rate	0.5
Xover chance	0.7
Generation gap	0.9

Particle swarm optimization (PSO)

The basic concept behind a PSO is that of an animal swarm on the search for food and the cooperative behaviour of the swarm's individuals to achieve their goal [S2, S3]. The individuals of the swarm (= particles in the PSO terminology) have a position p in the search space (here given by the combination of the four kinetic parameters of Eq. 19) and a velocity vector v. The food position is synonymous with the optimum of the objective function (here the *SSE* as defined in Eq. S-1). At first, the positions and the velocity of each particle is initialized to a random value. For the position the values are taken from the intervals given in Table S-1. For the velocity $\pm a$ is used as range for the random values where a is the half of the respective interval length from Table S-1. Then for each particle the objective function is evaluated. For those particles that reached a new personal best position the old one is replaced with the current position and likewise with the global best position. The updating functions for the velocity v and the position p are given by

$$v_i = f_d\left(v_i + c_1 r_{nd}\left(p_{best,i} - p_i\right) + c_2 r_{nd}\left(g_{best} - p_i\right)\right) \quad \text{(S-2)}$$

$$p_i = p_i + v_i \quad \text{(S-3)}$$

with the damping factor f_d, the learning coefficients c_1 and c_2, a random double between 0 and 1, r_{nd}, the best position for the i^{th} particle $p_{best,i}$, and the global best position g_{best}. Here the damping factor is set to 0.9. The consequence of this is that the velocities of all particles decrease during the iteration process ensuring algorithm convergence. The learning coefficients c_1 and c_2 can be used to adjust the influence of $p_{best,i}$ and g_{best}. For example with $c_2 > c_1$ all particles would have a higher tendency to move towards g_{best} resulting in fast convergence. But then a lower portion of the search space is scanned compared to the cases $c_1 = c_2$ or $c_1 > c_2$. In this study $c_1 = c_2 = 1.2$ was used. After applying Eq. S-3 all new position vectors are checked for bound violations and are limited to the ranges given in Table S-1 when indicated.

The evaluation of the objective function and the updating step is repeated until one of two stopping criterions is reached. The first stopping criterion is the maximum number of iterations, the second criterion is the minimum difference which refers to the absolute difference of two consecutive g_{best} values. The particle with the lowest error in the last iteration is then used as input to a simplex algorithm to ensure a local (or even the global) minimum is reached. The sequence of steps of the PSO is shown in Figure S-3.

Table S-3: Constants to control the PSO.

Parameter	Value
Number of individuals	10^{6}
Maximum numbers of iterations	10^{6}
Minimal difference	10^{-30}

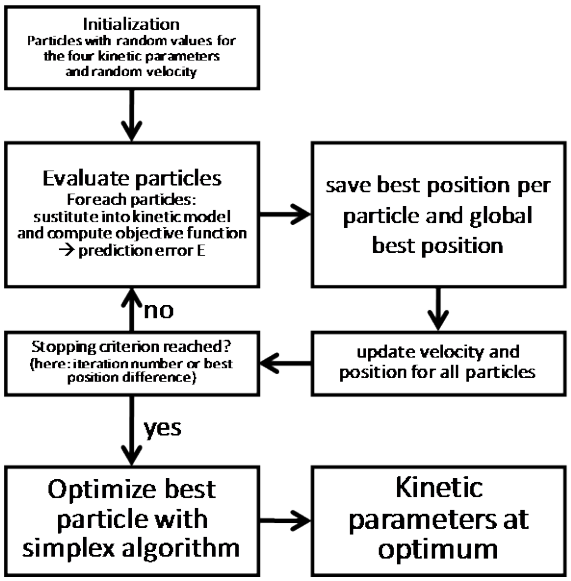

Figure S-3: Scheme of the parameter optimization employing a particle swarm optimization procedure (PSO).

Results of the optimization procedures

160 optimization runs were done using the GA and 1200 using the PSO, with the algorithm settings and parameter ranges given in the Tables S-1, S-2, and S-3. The best solution from all 1360 runs is given in Table S-4.

Table S-4. Results of the non-linear parameter optimization.

kinetic parameter	unit	value
χ_1	mol m^{-2} s^{-1}	$3.64\cdot10^{-7}$
χ_2	m^2 s mol^{-1}	$1.22\cdot10^{9}$
${}^{a}k_{NO}/(1+K_{H_2O}c_{H_2O})$	m s^{-1}	$1.08\cdot10^{-2}$
${}^{d}k_{NO}$	mol m^{-2} s^{-1}	1.00

Note: number of data = 54; *SSE* < $1.14\cdot10^{-14}$

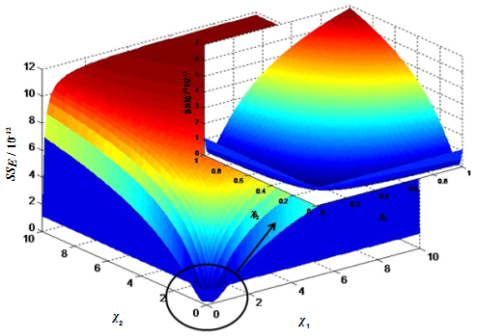

Figure S-4. 3D-Plot of the *SSE* for constant values of ${}^{a}k_{NO}/(1+K_{H_2O}c_{H_2O})$ and ${}^{d}k_{NO}$. The inset shows the region that probably contains the global optimum.

But many other solutions with *SSE* very close to $1.14\cdot10^{-14}$ but with a huge variance for the parameters, especially for χ_1 and χ_2, were found suggesting that only a number of local optima was found and that a change of algorithm settings and/or parameter ranges are necessary to achieve more reliable results.

To further examine this optimization problem the objective function *SSE* was visualized. This was done by (a) keeping χ_1 and χ_2 constant and generating 3D-plots of the objective function $SSE({}^{a}k_{NO}/(1+K_{H_2O}c_{H_2O}), {}^{d}k_{NO})$ and (b) keeping ${}^{a}k_{NO}/(1+K_{H_2O}c_{H_2O})$ and ${}^{d}k_{NO}$ constant and generating 3D-plots of $SSE(\chi_1, \chi_2)$. The most informative example of such a 3D-plot is presented as Figure S-4. As can be seen the error surface forms a plateau with an almost constant and high *SSE* for all parameter combinations where both χ_1 and χ_2 are much greater than 1. In contrast, for χ_1 and/or χ_2 being close to 1 exists a "curved valley" that probably contains the global optimum. This is in agreement with the results of the first optimization runs showing that solutions with small *SSE* only exist for low χ_1 and/or low χ_2 values.

This visualization allows to exclude all parameter combinations where both χ_1 and χ_2 are greater than 1 and to define two subsets with new intervals for the four kinetic parameters of Eq. 19 (Table S-4). For ${}^{a}k_{NO}/(1+K_{H_2O}c_{H_2O})$ and ${}^{d}k_{NO}$ no optimized parameter ranges could be deduced from the visualization of the *SSE*.

Table S-4: Subsets with new intervals for the parameters of Eq. 19 limiting the search space.

	Subset 1		Subset 2	
Parameter	Min.	Max.	Min.	Max.
χ_1	10^{-9}	10^{9}	10^{-9}	1
χ_2	10^{-9}	1	10^{-9}	10^{9}
${}^{a}k_{NO}/(1+K_{H_2O}c_{H_2O})$	10^{-9}	1	10^{-9}	1
${}^{d}k_{NO}$	10^{-9}	1	10^{-9}	1

In total 1360 optimization runs were performed using the intervals given of Table S-4 to generate the initial population (GA) and the initial particles positions (PSO). 680 runs were performed using subset 2 of Table S-4 resulting in the solution presented in Table 4 of the manuscript. This solution was found in 123 optimization runs. The majority of the remaining solutions are located in the proximity of that solution with small variations in the parameter values and slightly higher *SSE*. Therefore, it is assumed that the global optimum of the optimization problem is represented by the tabulated values.

These results show unambiguously that even if global optimization techniques are applied to a given problem it is vital to survey the error surface to be able to limit the search space when no *a priori* knowledge of the exact parameter ranges exists.

References

[S1] Automatic Control and Systems Engineering Group University of Sheffield (UK). Evolutionary Computation Research Team: Genetic Algorithm Toolbox. 2011. Available from: http://www.sheffield.ac.uk/acse/research/ecrg/gat.html.

[S2] D. Swagatam, A. Abraham and A. Konar, Swarm Intelligence Algorithms in Bioinformatics. *Stud. Comput. Intell.*, 2008, **94**, 113-147.

[S3] J. Kennedy and R. Eberhart, Particle swarm optimization. *Proc. IEEE Int. Conf. Neural Networks 1995*, 1995, **4**, 1942-1948.

III.

Recently, Hunger *et al.* [60] have employed a rate law having the mathematical form

$$ {}^{r}r_{NO} = k_{NO}\frac{K_{NO}c_{NO}}{1+K_{NO}c_{NO}} \qquad (2) $$

to analyze the kinetics of the photocatalytic NO oxidation over TiO_2-containing concrete. They reported an influence of the light intensity E on the rate constant k_{NO}. Despite the fact that their tabulated data show a decrease of the kinetic parameter K_{NO} with increasing light intensity E (see Figure S-5) the authors assumed that K_{NO} is not a function of E. Analyzing their experimental data (Table 5 and 6 in ref. [60]) with

$$k_{NO} = \chi_1^* \left(-1 + \sqrt{1 + \chi_2^* E} \right) \quad \text{(S-4)}$$

and

$$K_{NO} = \frac{{}^a k_{NO}^*}{{}^d k_{NO}^* + \chi_1^* \left(-1 + \sqrt{1 + \chi_2^* E} \right)} \quad \text{(S-5)}$$

by non-linear optimization resulted in the parameters presented in Table S-4. In one optimization procedure (run 1) the kinetic parameters χ_1^* and χ_2^* were calculated with equation S-4 and subsequently the missing parameters were optimized holding χ_1^* and χ_2^* constant. In a second procedure (run 2) the four kinetic parameters were conjointly calculated by non-linear regression.

Table S-4: Results of the non-linear parameter optimization of experimental data published by Hunger *et al*. [60].

Parameter	Units	run 1	run 2
χ_1^*	mg m^{-3} s^{-1}	0.028	0.42
χ_2^*	m^2 W^{-1}	9.9	0.17
${}^a k_{NO}^*$	s^{-1}	1.2	1.5
${}^d k_{NO}^*$	mg m^{-3} s^{-1}	0.11	0.18
slope (R^2)[a]	-	0.986 (0.995)	0.987 (0.929)
slope (R^2)[b]	-	0.989 (0.814)	0.990 (0.847)

Note: slope of the line through origin of a) $k_{NO,\,cal} = f(k_{NO,exp})$, b) $K_{NO,\,cal} = f(K_{NO,exp})$, and the respective correlation coefficients.

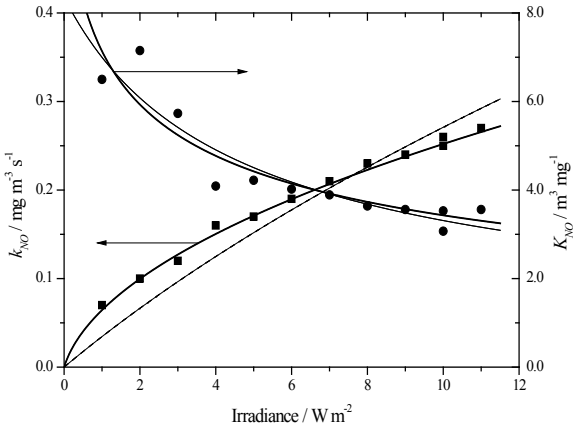

Figure S-5. Plot of the values of k_{NO} and K_{NO} published by Hunger et al. [60] vs. Irradiance. The solid lines have been calculated by inserting the kinetic parameters given in Table S-4 into the Equations S-4 and S-5.

Figure S-5 shows the values of k_{NO} and K_{NO} published by Hunger *et al*. [60] vs. irradiance as well as the graphs calculated with the Equations S-4 and S-5, and the optimized kinetic parameters given in Table S-4. A good agreement between experimental and calculated data becomes obvious clearly indicating that the rate law presented in Equation 19 is not only valid to describe the photocatalytic oxidation of nitrogen(II) oxide at the surface of Evonik-Degussa Aeroxide®TiO_2 P25.