Concerning "An Opinion on the Heterogeneous Photoreduction of N_2 with H_2O"

First Letter

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In a recent commentary, Edwards et al.[1] reported on the inefficiency in their attempts to photoreduce molecular nitrogen on heterogeneous surfaces. They used coprecipitated or surface-loaded iron-doped titania and certain single or binary oxide xerogels for performing two types of irradiation experiments in the presence of $N_{2(g)}$ enriched to 99% with ^{15}N and water vapor or liquid water. Though we accept the main conclusion of their work, namely that the authors were unsuccessful in photosynthesizing ammonia, in our opinion, on the basis of the results of their own negative experiments, Edwards et al. should question the reasons for their unsuccessful runs, instead of questioning the reproducibility of this intriguing reaction, which was first described in 1977[2] and which has since been reproduced in different laboratories[3, 4] under similar experimental conditions and with different TiO_2-based photocatalysts.

We believe that readers of Angewandte Chemie should be made aware of the fact Edwards et al. performed most of their experiments under conditions substantially different from those described in the literature and with different and inadequately characterized photocatalysts. Thus, most of their photoreduction experiments were conducted with "single or binary oxide xerogels" whose photocatalytic activity has not been documented in the scientific literature[5] and which, on the basis of our experience, are not expected to be photoactive. Moreover, the great majority of irradiation experiments were conducted in aqueous suspensions in which photoreduction of nitrogen is not generally observed. Only a total of twelve irradiation experiments were apparently performed with iron-doped TiO_2 powders of not reported composition and characterization which were allegedly prepared according to published procedures.[2, 3] We stress the point that the specimen preparation is crucial for the success of the process; this is why all papers in the field of heterogeneous catalysis report details on the specimen preparation and characterization. All researchers working in heterogeneous catalysis are well aware that an undetected contamination can invalidate all the findings. For the preparation of photocatalytically active TiO_2 powders, the iron-doped anatase must be subjected to a heat-treatment to effect a rearrangement of anatase into rutile. This requires carefully controlled conditions, since it is accompanied by drastic changes in crystal sizes and surface areas (see e.g., refs.[3, 6]). It is difficult to assess whether Edwards et al. had catalytically active powders as they did not provide details such as the rutile/anatase ratio, particle size, or the surface areas. Neither were specifications given for the photoreactivity runs. The reacting conditions such as mass of catalyst, time of irradiation, irradiated surface area of catalyst, temperature inside the photoreactor, and method of avoiding warming of catalyst due to the IR radiation of the 450 W lamp used were absent. The authors worked in batch vessels of quartz, which thus were more UV-transparent than our Pyrex vessels or our Pyrex continuous photoreactor. This may have favored the photooxidation of ammonia which becomes a side reaction especially after longer irradiation periods.

The authors are certainly correct in warning against ammonia contamination problems. However, it must be stressed that although contamination could explain random results, it could not explain trends in photoreactivity or changes in activity in response to changes in operating conditions or photocatalyst composition.[3] We call to mind the experiments[3] in which cycles of activation–deactivation of photocatalyst were clearly observed and also explained on the basis of ESR spectra performed contemporaneously with the photoactivity experiments. Only an "intelligent" contamination could explain all the results obtained in the field of dinitrogen photoreduction.

In discussing the possibility of direct nitrogen photooxidation reactions, a previously published paper should have been quoted.[7] Last but not least, the remarks made by Edwards et al. on the photoreduction of nitrogen on desert sands are quite unfounded as Schrauzer et al.[8] clearly explained how they calculated the ammonia yields from their $^{15}N_2$ experiments. Moreover, they also reported the yields of nitrogen photooxidation products, and already pointed out that ammonia photooxidation occurs as a side reaction.

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[4] H. Miyama, N. Fuji, Y. Nagao, *Chem. Phys. Lett.* **1980**, *74*, 523.

[5] In [1] the patent literature quoted is obviously in error: US 4688522, **1987** and US 4799870, **1989** are by H. A. McMaster but do not deal with photoreduction reactions. These patents deal with "Fluid Power Transfer Devices", a totally unrelated matter in our opinion.

[6] G. N. Schrauzer, T. D. Guth, J. Salehi, N. Strampach, Liu Nan Hui, M. R. Palmer in *Homogeneous and Heterogeneous Photocatalysis*, (Eds.: E. Pelizzetti, N. Serpone), D. Reidel, Dordrecht, **1986**, p. 509.

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