Optimizing photocatalytic oxidation for purifying air

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Finding optimal reaction conditions for TiO₂ photocatalysts is aided by molecular understanding of rate-determining steps and the factors that control them.

Gas-phase heterogeneous photocatalysis presents an attractive method for purifying air.¹⁻³ Light illumination of particulate metal oxides offers an especially cost effective and environmentally sound route for degrading pollutants that does not require unstable and potentially dangerous chemical oxidants, but only airborne oxygen. A major benefit of photocatalysis is that, powered by light, it can activate processes not thermally accessible under ambient conditions.

We presently have a thorough understanding of the photocatalytic action of semiconducting metal oxides, especially TiO₂.⁴,⁵ Photocatalysis in the aqueous phase has also been extensively studied. Less attention has been accorded the corresponding gas-solid reactions, although interest in gas-phase heterogeneous photocatalysis is growing. Over the past two decades it has become apparent that photosensitized gas-solid reactions can be one order of magnitude larger than the corresponding liquid-solid phase reactions, with quantum efficiencies on the order of 1%.⁴,⁵ Concomitant interest in gas-solid applications in air- and self-cleaning devices has enlarged the field considerably.³ Before photocatalysis can be considered a viable commercial alternative in self-cleaning applications, the issue of deactivation must be resolved.² At the same time, it is essential to identify rate-determining steps and to devise new methods and materials to improve photocatalytic efficiency.

We recently showed that the rate-determining step in the photocatalytic degradation of hydrocarbons on TiO₂ is the oxidation of stable surface-bound intermediates.⁶⁻⁸ It is well known that surface compounds with a carboxylic group (R-CO₂⁻) readily form on metal oxides. Indeed, even in the 1960s organics were thought to react stoichiometrically with metal oxides such as TiO₂ and ZnO.⁹

Using advanced in situ molecular spectroscopy for a wide range of particulate TiO₂ systems (with particles ranging from a few to several hundred nanometers), we have scrutinized the bonding of key intermediates typically found on TiO₂. Our results show unequivocally that the surface concentration of intermediates, notably so-called bridging bidentate R-CO₂⁻ (see Figure 1), depends on both crystal modification and particle size. Interestingly, the rate-determining steps differ for the various crystal modifications. Our simultaneous analysis of the gas-phase products demonstrates the significance of these findings. Photo-oxidation of propane indicates that the surface carbon mass balance deduced from mass spectrometry measurements will scale proportionally to the concentration of surface intermediates. Moreover, intermediate-sized anatase particles (∼25nm) are the most reactive.⁶⁻⁸ Thus, judicious choice of the photocatalyst makes it possible to control reactivity.

Correlation of reactivity with surface structure and bonding of intermediates to the photocatalyst can be extended to predict the optimum photo-oxidation catalyst for a large class of hydrocarbons. It is also possible to use this knowledge to suppress the formation of unwanted intermediates. We have found that it is possible to reduce the R-CO₂ concentration and at the same time maintain an efficient conversion rate. Addition of...
approximately a monolayer of water to the photocatalyst surface will ‘shield’ exposed Ti metal cation sites, which would otherwise be engaged in metal-oxygen bonding with R-CO$_2^-$ species (Figure 1, left). Any monodentate coordinated species that form (Figure 1, middle) are photo-oxidized much more rapidly than bridging species.$^{10}$ Overall, this results in reduced concentration of surface intermediates. Appropriate water concentration is important to maintain an effective photocatalytic reaction rate. Too much water results in inefficient coupling of the radicals created at the TiO$_2$ surface with the pollutant embedded in the water layer (Figure 1, right). It is also possible to combine the photocatalytic action with thermally driven processes, and to adjust the temperature of the photocatalyst to optimize both water surface concentration and thermal reactions (Figure 2). By doing so, a suitable window can be created in the relative humidity and temperature space that maintains the appropriate water concentration and, at the same time, speeds up the thermal processes.$^{8,11}$

TiO$_2$ requires UV light, and much research in photocatalysis is currently aimed at finding new catalysts that are active in the visible light region. Results of our research, however, draw attention to classical problems in heterogeneous catalysis, including appropriate surface-adsorbate bonding (Sabatier’s principle). In addition, our finding that controlled reaction conditions can improve photocatalytic conversion is of immediate practical importance.

![Figure 2. Gas-phase photo-oxidation of propane on 7nm anatase TiO$_2$ (500ppm in a feed of synthetic air of 100ml/min) is shown here as a function of temperature of the photocatalyst ($T_{cat}$) and relative humidity (RH). Adapted from refs. 8 and 11.](image)

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**References**

8. L. Österlund, *Swedish patent no. 0501169-7*.