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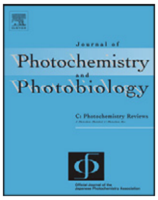

Review

Unravelling the mysteries of gas phase photocatalytic reaction pathways by studying the catalyst surface: A literature review of different Fourier transform infrared spectroscopic reaction cells used in the field

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ABSTRACT

Unlike the profound knowledge of the reaction mechanisms occurring in water phase photocatalysis, still fairly little is known on the reaction mechanisms occurring on the catalyst surface when dealing with gaseous pollutants. Unfortunately, there are some differences between both reactions. For one, there are no abundant hydroxyl radicals present in the gas phase, so that possibly other species prove to be important in abating the pollutant. In order to unravel the mysteries of gas phase photocatalytic reaction pathways, in situ techniques must be used to allow the detection and identification of reaction intermediates on a working catalyst. Several techniques were already used in the past, of which Fourier transform infrared spectroscopy seems to be the most versatile. This review will therefore give a selective overview of different spectroscopic reaction cells constructed for the in situ study of photocatalytic gas phase reactions.

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1. Introduction

Heterogeneous photocatalysis is a technique that has received a lot of scientific attention since it was first discovered by Fujishima and Honda in 1972 [1]. It is an intensive research area for the removal of environmental threatening and toxic components from water and polluted air [2–9]. There are, however, still some general issues concerning photocatalysis, like the relatively low photonic efficiency for most degradation processes [10] and the limited flux of ultraviolet photons [11]. Additionally, another concern is the possible deactivation of the catalyst [12–15]. When an adsorbed pollutant is oxidised, it is not imaginary that one of the formed intermediates sticks on the surface, hereby blocking adsorption sites. Eventually, this might lead to a deactivated catalyst [16]. Furthermore, photocatalysis is generally a non-selective method and although this lack of sensitivity might be advantageous in some cases, a poor selectivity also implies that the catalyst does not differentiate between highly hazardous pollutants and pollutants of low toxicity. It may even be the case that the degradation products can be more dangerous than the initial compound [10]. It is therefore very important to study the photocatalytic reaction pathway and gain information on whether or not potential intermediates remain on the surface to deactivate the catalyst.

Several studies to obtain information of the photocatalytic reaction pathway have been performed throughout the years. Many different techniques have been used, amongst others: nuclear magnetic resonance (NMR) [17–19], temperature-programmed oxidation (TPO) [20,21], transmission electron microscopy (TEM) [22], gas chromatography (GC) [23–25], photoacoustic spectroscopy (PAS) [26], Raman spectroscopy [27,28] and IR spectroscopy [29–31]. In order to focus, this literature review will only discuss the latter technique, which seems to be the most versatile one.

Photocatalysis can be used for both water and air purification purposes, but although the general working mechanism is similar for both, there are still a lot of differences between the two approaches. In the case of water purification, there can be some adsorption issues due to the abundant presence of water, which can block the adsorption sites [10]. On the other hand, this water can initiate the formation of hydroxyl radicals, which can be used to abate the present pollutants [32]. For gas phase photocatalysis, the situation is somewhat different. Although hydroxyl radicals are very useful in this state of matter as well, the amount of water is rather limited [11]. However, the amount of O_2 present in air is rarely limiting. The present O_2 can therefore be used to form superoxide radical anions, which in turn can be used to oxidise the pollutants [33]. Since we will focus on IR spectroscopy in this review, we have opted to use this technique to elucidate gas phase photocatalytic reactions. This choice is given by the fact that water has a strong interference with IR, resulting in a very difficult use of the technique. As a result, gas phase photocatalytic reaction mechanisms in the presence of large amount of water vapour still remains speculative.

2. Photocatalysis

Photocatalysis is a process where light is used to activate a catalyst to improve certain reactions in order to abate air and water pollution. The most widely used photocatalyst is the n-type semiconductor, titanium dioxide (TiO_2). It is an interesting catalyst due to its chemical stability, non-toxicity and low cost [34,35]. The general working principle of photocatalysis is fairly known and is the same in water and air. The process is initiated by activating the catalyst with light with sufficient energy, commonly this is ultraviolet (UV) light. When this happens, an electron is excited from the filled valence band to the empty conduction band, leaving behind a hole in the valence band (Fig. 1 inset and (p)). An electron–hole (e^-–h^+) pair is thus generated (reaction (1)) [36], which can recombine again (either in bulk ((r) in Fig. 1) or on the surface ((q) in Fig. 1)) or which can migrate toward the catalyst surface and initiate redox reactions to reduce ((s) in Fig. 1) or oxidise ((t) in Fig. 1) the pollutants [10,33,36].

There are thus two distinct species present: a hole and an electron. The following reactions represent a couple of the possible reactions of e^- and h^+ on the surface, initiating reactive species [33].

$$TiO_2 + h\nu \xrightarrow{h\nu > E_g} TiO_2(h^+ + e^-) \tag{1}$$

$$TiO_2(h^+) + {}^-OH_{(ads)} \rightarrow TiO_2 + OH^{\bullet}{}_{(ads)} \tag{2}$$

$$TiO_2(e^-) + O_{2(ads)} \rightarrow TiO_2 + O_{2(ads)}{}^{\bullet -} \tag{3}$$

The hole can react on the surface with adsorbed water or surface hydroxyl groups in order to form hydroxyl radicals (reaction (2)) [10]. These radicals are postulated to be very important for the oxidation processes because of their large activity [11]. There seems to exist a widespread agreement on the major role in TiO_2 photocatalysis of these hydroxyl radicals generated by adsorbed water species on the TiO_2 surface [10,37–39]. Despite this consensus, several studies have questioned whether this mechanism is indeed reasonable to all TiO_2 photocatalytic oxidation reactions [40–45]. Yates and co-workers [41–43] reported that hydroxyl radicals did not play such an important role in the photocatalytic degradation of pollutants, like trichloroethylene [41] and acetonitrile [42], while Yu and Chuang [44] stated that coverage of ethanol on TiO_2 is the determining factor of the oxidation process. They found that, at low ethanol coverage, hydroxyl radicals were the key oxidising particles, while at high ethanol coverage the photogenerated holes take the lead in the oxidation. Similarly, Ishibashi et al. [45] reported, by measuring the quantum yield of formation of hydroxyl radicals by means of a fluorescence probe method, that the formation of these radicals was not of major importance on irradiated TiO_2 in aqueous solutions. Furthermore, research conducted in the groups of Salvador and Nakamura [46–48], amongst others, have shown that water molecules adsorbed on terminal Ti atoms cannot be photo-oxidised with valence band holes. From these studies, it was concluded that free hydroxyl radicals can only be generated by the electroreduction of oxygen with photogenerated