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Photocatalytic oxidation of butyl acetate in vapor phase on TiO_2, Pt/TiO_2 and WO_3/TiO_2 catalysts

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Abstract

The photocatalytic degradation of butyl acetate in the gas phase was investigated in a fixed-bed continuous annular reactor using a titanium dioxide semiconductor, Pt/TiO_2 and WO_3/TiO_2 catalysts. Platinum was deposited on the titanium by adsorption of $PtCl_6^{2-}$ anions, and WO_3/TiO_2 was prepared by a conventional impregnation method using an aqueous solution of ammonium paratungstate. Different samples, with different nominal weight loadings in Pt and WO_3, were tested. For each catalyst sample studied, air containing butyl acetate and water vapors in various molar ratios was fed at 200 cm^3/min to the photoreactor. The roles of the reaction temperature and of H_2O in the photocatalytic oxidation of butyl acetate and the influence of the content of TiO_2, Pt, and WO_3 were investigated. Although an initial decay in photocatalytic activity was observed, partly issued from an initial deactivation, total mineralization was achieved under all experimental conditions. For relative water humidity between 50 and 75% and for adequate TiO_2 covering ratios, the photocatalytic activity of TiO_2 toward the photocatalytic degradation of butyl acetate can be greatly improved by the addition of WO_3, mainly due to a prevention of the initial deactivation and of photogenerated charge recombination. This optimized photocatalyst is very stable on stream and no regeneration treatments are needed. The influence of Pt and WO_3 on photocatalytic activity are discussed with regard to chemical and electronic modifications of TiO_2.

Keywords: Photocatalytic oxidation; Butyl acetate; Total mineralization; Pt/TiO_2; WO_3/TiO_2; Chemical and electronic modifications

1. Introduction

Volatile organic compounds (VOCs) are an important class of pollutants usually found in the atmosphere of all urban and industrial areas. The TiO_2-mediated heterogeneous photocatalysis for the oxidation of these organic compounds at low concentrations has been extensively studied for environmental decontamination purposes [1–3]. Photocatalysis on TiO_2 is advantageous compared to other oxidation methods because it takes place at room temperature, so no thermal activation is necessary and only low-intensity UV lights are needed. Moreover, TiO_2 is an inexpensive photocatalyst. While most relevant studies have been concerned with photodegradation in the liquid phase, the degradation of gaseous organic compounds has gained importance recently [4,5], although some pioneering and earlier studies [6–8] of heterogeneous gas phase systems were conducted previously. Photocatalysis requires illumination with photons having energy greater than the band gap of the semiconductor. For TiO_2, photoexcitation across the band gap requires wavelengths less than about 385 nm, which corresponds to near-UV illumination. Absorption of UV light will excite electrons from the valence to the conduction band, creating electron–hole pairs. These electron–hole pairs can recombine or diffuse to the surface where they can initiate redox reactions with surface species. Unfortunately, surface or volume charges recombinations will hinder the photocatalytic phenomenon.

TiO_2 shows the highest quantum yield among the popular semiconductors [9]. However, in many cases, the photocatalytic activity of TiO_2 is not enough to be useful for industrial purposes. Therefore, several methods to improve the photocatalytic efficiency of TiO_2 such as increasing the external surface area, modifying the structural and surface morphological properties, or generating structure defects in TiO_2 have been attempted [10,11]. For other purposes, many studies have been focused on methods to support TiO_2 photocatalysts. Thus attempts to prepare supported TiO_2 cata-

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lysts using fiber glass [12], honeycomb [13], activated carbon [14], and zeolites [15] as material support have been made; in these two last cases, the aim was to associate a very porous and high-adsorption-capacity support to TiO_2 to increase the pollutant adsorption capacity.

So far, it has been shown in the literature that modifications of the TiO_2 surface with metals [16], metal oxides [17], or other semiconductors [18] are some of the most successful ways to improve photocatalytic activity for the photooxidation of some organic products mainly in aqueous media. With regard to the loading of metal oxides, a beneficial influence of the addition of WO_3 or MoO_3 [17,19] on TiO_2 has already been observed for the occurrence of some photocatalytic processes, such as photooxidation of methanol [17] and 1,4-dichlorobenzene [20,21], and photodegradation of 4-nitrophenol [10] in aqueous media. Some examples have been reported also in gas phase for photooxidation of 2-propanol and benzene [22].

With regard to the influence of the addition of metals, some authors demonstrated that a few metals, such as Ag, Pd, Au, and Pt, could improve the photocatalytic activity of TiO_2. However, the case of Pt is much more debated. According to some authors, addition of Pt in the liquid phase has been found to improve photocatalytic efficiencies [23] in many oxidation reactions, demonstrating the electron-trapping effect of noble metals. Nevertheless, the addition of Pt was scarcely used for gaseous stream treatment and, in these cases, the influence of Pt is much more subtle and delicate [24,25], depending mainly on experimental conditions.

The present paper reports and compares the photocatalytic activity of TiO_2, Pt/TiO_2, and WO_3/TiO_2 systems toward butyl acetate degradation in vapor phase. Different catalysts, varying by their TiO_2 covering ratios and Pt and WO_3 loading, have been tested and compared at room temperature and at 100 °C for various humidity ratios. The aim of this study was to improve the photocatalytic activity of TiO_2 in gas phase, focusing only on chemical and electronic modifications through the addition of Pt and WO_3, which until now have remained scarcely used for gaseous stream treatment. The effect of WO_3 and Pt modifications of photocatalytic activity will also be discussed.

2. Experimentals

2.1. Experimental device and procedure

The photocatalytic reactor used is a cylindrical concentric Pyrex-quartz tubular reactor (length 300 mm, internal diameter 35 mm), as represented in Fig. 1. The reactant mixture flows between the first internal (quartz) and the second external (Pyrex) concentric tubes, set 4 mm apart. The UV light source is a commercial 8-W black-light tube with a spectral peak at around 350 nm. As represented in Fig. 2, the initial air flow is separated into three path ways, each one controlled by a separate mass flow controller. Air is continuously bubbled through two saturators, one containing the organic compound and the other one containing the water. The butyl acetate/air/water mixture in various concentrations flowed at 200 cm^3/min. After reaction, the products were analyzed by a thermal conductivity detector (microchromatograph HP microCG M200H) equipped for H_2O and CO_2 quantification.

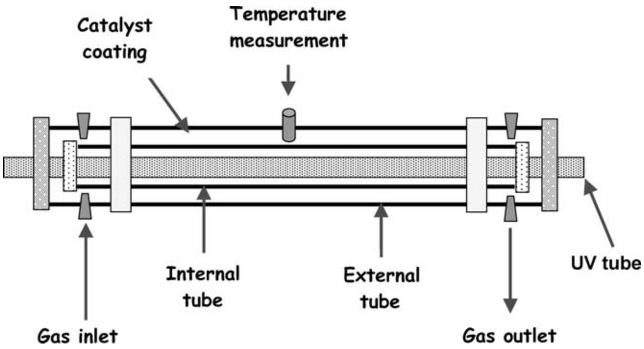


Fig. 1. Photocatalytic annular concentric reactor.

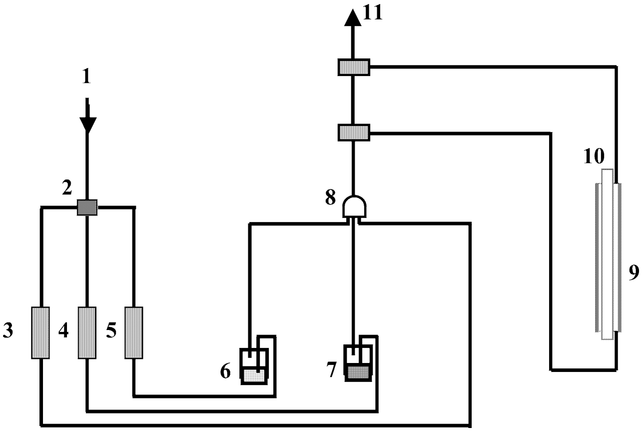


Fig. 2. Photocatalytic device. (1) Air arrival, (2) mixing system, (3) dry air, (4) air + H_2O, (5) air + VOC, (6) VOC saturator, (7) H_2O saturator, (8) mixing system, (9) photocatalytic reactor, (10) UV lamp, (11) microchromatography.

The catalyst was treated initially under 200 cm^3/min dry air at room temperature for 30 min and then irradiated at reaction temperature for 15 min before the reaction mixture was switched on. Relative humidity of 100% is defined as the saturated vapor pressure of water at 25 °C, which corresponds to about 24 Torr (about 3% relative to the total atmospheric pressure).

The carbon deficit (expressed in ppm) has been defined as the amount of carbon remaining adsorbed on the catalyst surface. It is expressed as:

$$\text{Carbon deficit } (t) \text{ (ppm)} = p^i - \sum_j \alpha_j \times p_j(t),$$

where p^i is the initial acetate butyl pressure, j is the carbonaceous compound in the gas phase, α_j is the stoichiometry factor of the j compound, and $p_j(t)$ is the partial pressure (or concentration) of each compound in the gas phase.

2.2. Materials and catalyst preparation

The reactant, butyl acetate ($\gg$ 99%) was purchased from Aldrich and used without further purification. The titania support is a P-25 from Degussa: 85% anatase, 15% rutile, $S_{\text{BET}} = 50\ \text{m}^2/\text{g}$. Uniform TiO_2 film deposition was achieved by evenly distributing a TiO_2 slurry inside the Pyrex reactor and evaporating the slurry to dryness while continuously spinning the glass tube. Pt/TiO_2 and WO_3/TiO_2 were prepared by adding subsequently appropriate amounts of $H_2PtCl_6 \cdot 6H_2O$ and $(NH_4)_{10}H_2(W_2O_7)_6$, respectively, and evaporating the solvent until dryness. After that, both types of samples were heated overnight at 120 °C and calcined at air at 420 °C for 1 h. In the case of Pt/TiO_2 catalysts, preparation continued with a thermal reduction treatment of 1 h at 420 °C. Different Pt/TiO_2 and WO_3/TiO_2 samples were prepared with contents varying from 1 to 10% (weight).

3. Results

3.1. Optimization of TiO_2 recovering ratio on the Pyrex support

Optimization of TiO_2 content toward photocatalytic degradation of butyl acetate was carried out at room temperature at 200 cm^3/min at a relative humidity ratio of 25% and a reactant concentration of 500 ppm. Fig. 3 represents the evolution of total conversion in function of TiO_2 content, i.e., the recovering ratio of the coating on the inside wall of the external Pyrex tube. It can be observed that the maximum photoactivity for the oxidation of butyl acetate was obtained for a weight loading of TiO_2 on the Pyrex glass surface of 0.23 mg/cm^2. Below this value, it can be supposed that the Pyrex support is not completely covered by TiO_2. On the other hand, higher values result in a slight diminution of total conversion. All the other experiments on Pt/TiO_2 and WO_3/TiO_2 described in this paper were carried out in the same manner, in each case after optimization of the recovering ratio of the catalyst, which of course was specific for each catalyst.

3.2. Photocatalytic oxidation of butyl acetate on TiO_2

3.2.1. Influence of relative humidity on catalytic activity and on deactivation

Fig. 4 shows the evolution of the total conversion as a function of time on stream at room temperature starting from 500 ppm of pollutant with relative humidities of 0, 25, 50, 75, and 95%. Whatever the water content, it must be noted, that, photocatalytic oxidation of butyl acetate leads to a complete mineralization into CO_2 and H_2O without formation of by-products, according to the following equation:

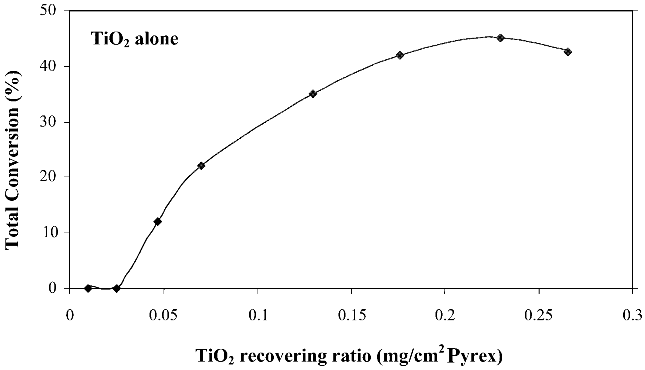


Fig. 3. Evolution of the total conversion (%) versus TiO_2 coating recovering ratio (mg/cm^2 Pyrex).

$$C_6H_{12}O_2 + 8O_2 \rightarrow 6CO_2 + 6H_2O.$$

A curve representing an example of CO_2 formation during the photooxidation of 500 ppm of butyl acetate on TiO_2 at room temperature and 25% relative humidity is given in Fig. 5.

The initial conversion is very high (near 100%) and a rapid decay of activity occurs in the first minutes on stream to reach a stable value for conversion under steady state conditions. This initial decrease of activity can be due either to an initial conditioning or to a poisoning of the surface. More detailed studies have revealed that this initial loss of total activity is conditioned mainly by two factors, the relative humidity ratio and an inhibition effect due to carbonaceous species. Concerning the relative humidity ratio, it can be observed in Fig. 6, which is an enlargement of Fig. 4 during the first minutes on stream, that the initial diminution in activity decreases while the water content increases from 0 to 75%. The second assumption about poisoning by carbonaceous species is confirmed in Fig. 7a, showing the carbon deficit related to the experiment corresponding to Fig. 4c, in which an initial carbon deficit

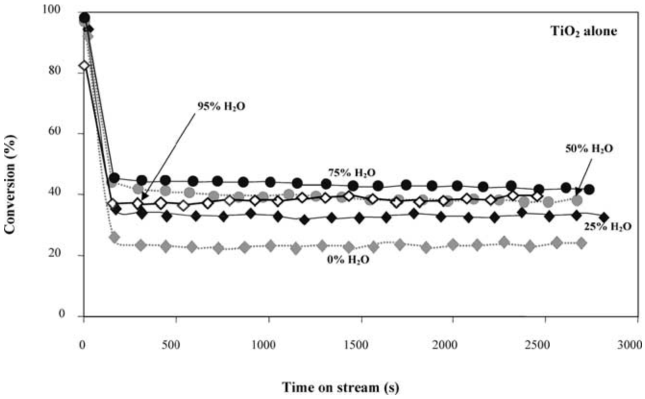


Fig. 4. Evolution of the total conversion (%) for the photooxidation of 500 ppm butyl acetate on TiO_2 at room temperature versus time on stream (s).

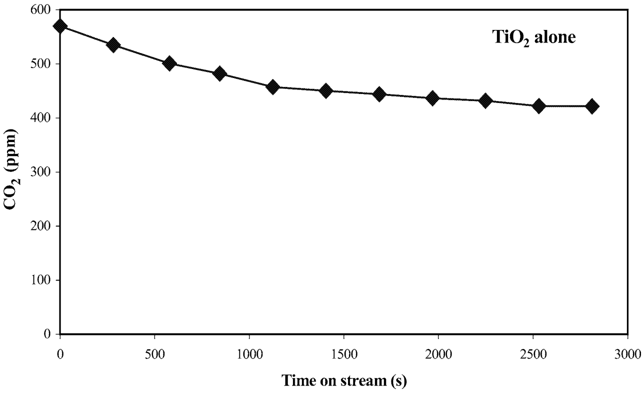


Fig. 5. Evolution of the CO_2 formation during the photooxidation of 500 ppm butyl acetate on TiO_2 at room temperature versus time on stream (s) at 25% relative humidity.

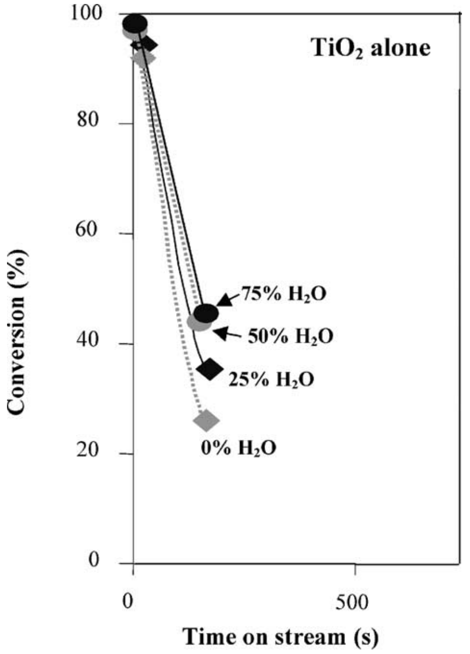
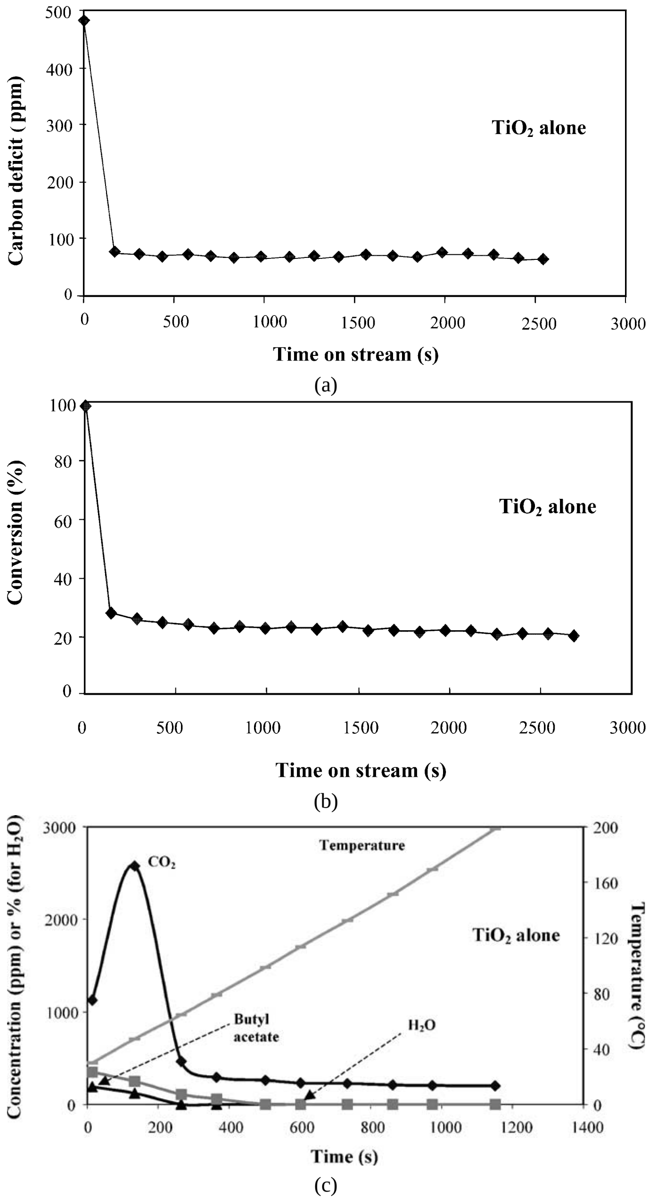


Fig. 6. Comparison of the decay of initial activity for the photooxidation of 500 ppm butyl acetate at room temperature on TiO_2 during the first minutes on stream (s).

has been detected; this carbon deficit falls in with the initial decay in photocatalytic activity. At this stage, it can be supposed that the effect could be due either to a strong adsorption of the reactant or one of the product, CO_2, formed in high amounts at the very beginning of the photocatalytic reaction, or to an adsorption of carboxylate or other carbonaceous species yielding a blocking of a part of the surface sites. Fig. 7b, showing the diminution of catalytic activity after addition of 1150 ppm CO_2 in the reactant mixture, suggests that CO_2 has an inhibition effect on photocatalytic activity of butyl acetate oxidation on TiO_2. This is confirmed in Fig. 7c, representing the desorption profiles obtained during heating from room temperature to 200 °C in the dark (UV off) under dry air and carried out after the photocatalytic test. During this desorption phase, essentially only a CO_2 desorption peak and negligible amounts of butyle acetate and H_2O are observed.



(a)

(b)

(c)

Fig. 7. (a) Evolution of the total carbon deficit (ppm) during the photooxidation of 500 ppm butyl acetate at room temperature (50% humidity) on TiO_2 versus time on stream (s). (b) Evolution of the total conversion (%) for the photooxidation of 500 ppm butyl acetate at room temperature (50% humidity) on TiO_2 in the presence of 1150 ppm CO_2 in the reactant feed versus time on stream (s). (c) Desorption profiles on TiO_2 in the dark (UV off) during heating from room temperature to 200 °C under dry air after photocatalytic test.

It must be noted that the very high initial activity of TiO_2, approaching 100% (before the activity decay), could be restored after regeneration under dry air in UV illumination, at room temperature or even more easily at higher temperature, around 100 °C.

The increase of humidity ratio from 25 to 75% results not only in a decrease in the initial activity loss but also in a conversion enhancement after stabilization in steady-state conditions. Thus, the optimal range of humidity is situated between 25 and 75% under our experimental conditions, the effect becoming detrimental with a further increase of water content.

3.2.2. Influence of reaction temperature

In Fig. 8 showing the evolution of the total conversion as a function of time on stream at 100 °C starting from 500 ppm pollutant with relative humidities of 0, 25, 50, and 75%, it can be observed that the increase in reaction temperature from room temperature to 100 °C yields an enhancement of the photocatalytic activity. This improvement of the photocatalytic activity is perceptible simultaneously on the initial activity decay and on the conversion under steady state conditions, the first parameter being lowered and the second parameter being increased. However, with water added to the reaction mixture, the variation of these two parameters has only a slight influence on photocatalytic activity, at 100 °C than at room temperature.

Thus, it can be supposed, according to Fig. 7c, that the main effect of the reaction temperature increase is to promote the desorption of CO_2, leading to a decrease of its poisoning and inhibition effect of the surface.

It must be mentioned that no evolution in product selectivities has been detected between room temperature and 100 °C; whatever the reaction temperature, total mineralization can be achieved.

3.3. Photocatalytic oxidation of butyl acetate on TiO_2 modified by Pt

The addition of 1% (weight) Pt on TiO_2 (Fig. 9) yields a decrease in the photocatalytic activity at room temperature as compared to that obtained on TiO_2, although total mineralization of the reactant into CO_2 and H_2O can be achieved. However, the lower photocatalytic activity in comparison to that obtained on TiO_2 may not result from a most important initial decay in conversion. Indeed, the increase of reaction temperature from room temperature to 100 °C has no real effect (Fig. 9) on the improvement of photocatalytic activity toward butyl acetate oxidation as was the case on TiO_2 without Pt. In the same manner, complementary experiments have shown that there is no effect either of the relative humidity or of the Pt content, varying from 1 to 10% (weight). Reactions performed in the dark (UV off) do not lead to oxidation of butyl acetate either at room temperature or at 100 °C; thus Pt is not active for classical thermal catalytic oxidation at these temperatures.

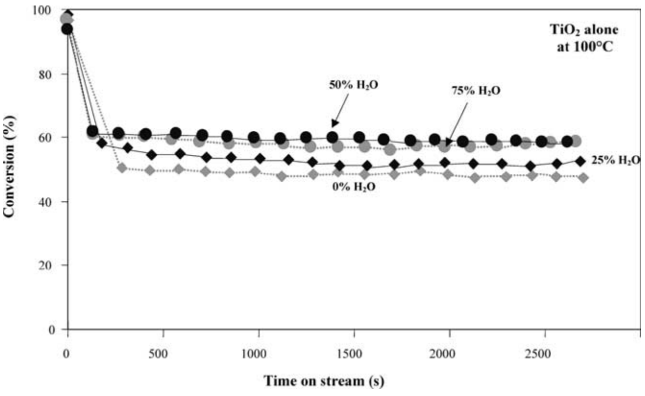


Fig. 8. Evolution of the total conversion (%) for the photooxidation of 500 ppm butyl acetate on TiO_2 at 100 °C versus time on stream (s).

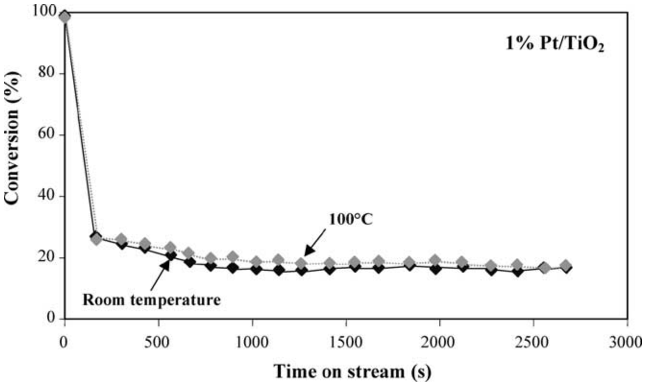


Fig. 9. Evolution of the total conversion (%) for the photooxidation of 500 ppm butyl acetate on 1% Pt/TiO_2 (50% humidity) versus time on stream (s).

3.4. Photocatalytic oxidation of butyl acetate on TiO_2 modified by WO_3

3.4.1. Influence of relative humidity on catalytic activity and on deactivation

The addition of 1% (weight) of WO_3 on the previous TiO_2 catalyst yields a considerable enhancement of photocatalytic activity for butyl acetate oxidation (Fig. 10), keeping the total mineralization in CO_2 and H_2O at room temperature. The influence of relative humidity on catalytic activity is more important than it was in the case of TiO_2 alone, especially by increasing the water content from 0 to 25 and 50%. After that a greater water content only slightly increases the photocatalytic activity.

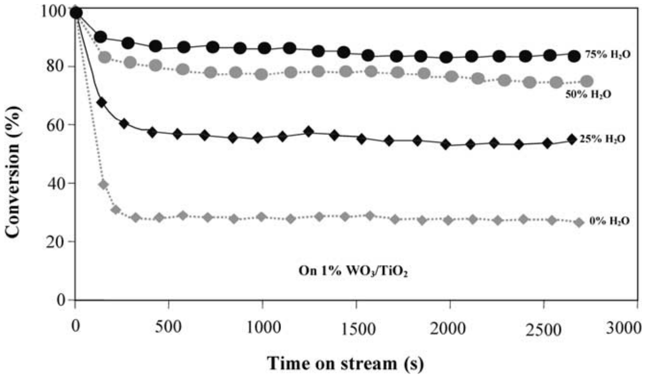
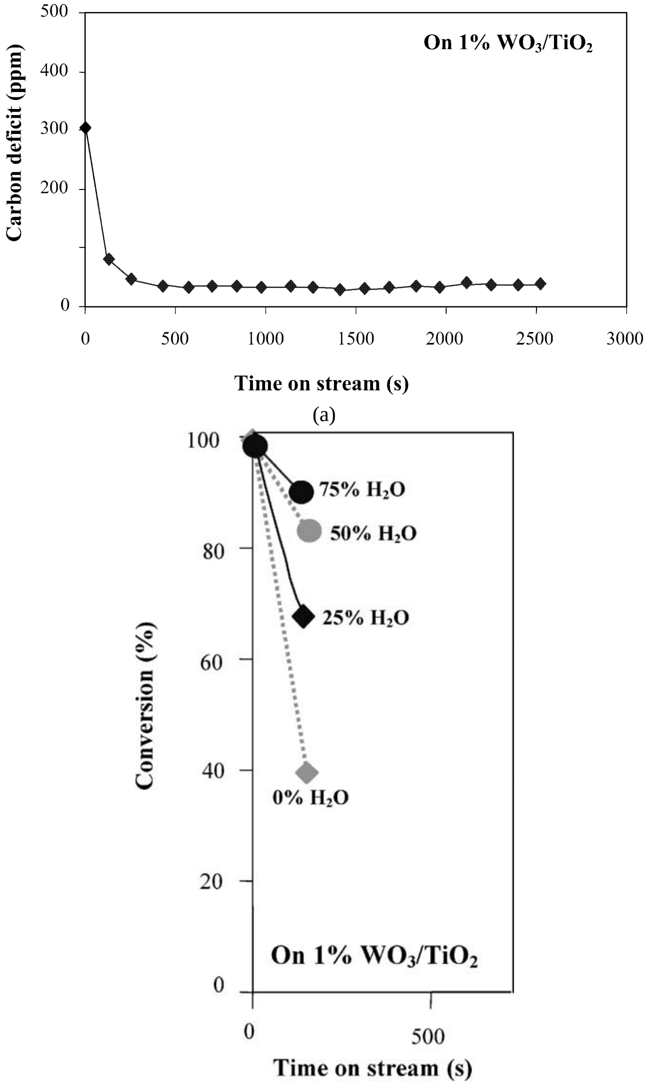


Fig. 10. Evolution of the total conversion (%) for the photooxidation of 500 ppm butyl acetate on 1% WO_3/TiO_2 at room temperature versus time on stream (s).

Comparing in more detail the initial decrease of activity on 1% WO_3/TiO_2 and TiO_2 leads to the observation that it is limited in the former case. This observation is correlated with the fact that the carbon deficit (Fig. 11a), related to the experiment corresponding to Fig. 10, is lowered. Moreover, the effect of the decrease of initial loss of activity as a function of water content is much more pronounced than that on TiO_2 alone (Fig. 11b). In the same manner, for the same water content, the initial decay of activity is less important on 1% WO_3/TiO_2 than on TiO_2 alone (compare Fig. 11b with Fig. 6). WO_3 contents from 1 to 10% (weight) have been tested. It has been observed in this regard that the best photocatalytic value was obtained for 4% WO_3/TiO_2, as represented and compared in Fig. 12 for 50% humidity.



(a)

(b)

Fig. 11. (a) Evolution of the total carbon deficit (ppm) during the photooxidation of 500 ppm butyl acetate at room temperature (50% humidity) on 1% WO_3/TiO_2 versus time on stream (s). (b) Comparison of the decay of initial activity for the photooxidation of 500 ppm of butyl acetate at room temperature on 1% WO_3/TiO_2 during the first minutes on stream (s).

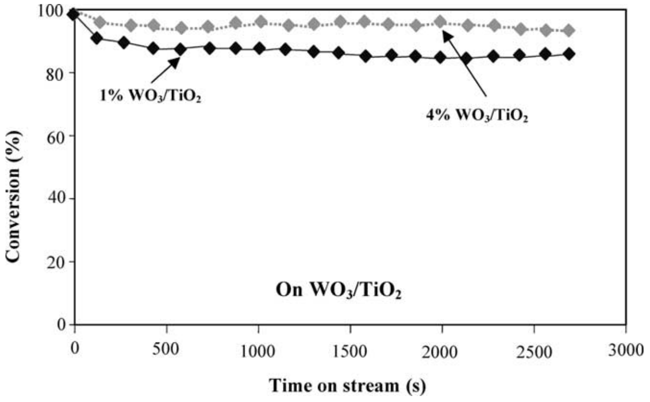


Fig. 12. Influence of the WO_3 content on the evolution of the total conversion (%) for the photooxidation of 500 ppm butyl acetate at room temperature (50% humidity) versus time on stream (s).

3.4.2. *Influence of reaction temperature*

Contrarily to TiO_2 alone, the increase of reaction temperature from room temperature to 100 °C does not result in an improvement of photocatalytic activity (Fig. 13) even by changing the relative humidity ratio but it leads to a degradation of total activity. However, at this reaction temperature total mineralization in CO_2 and H_2O was achieved. These experiments have been followed by a decrease of reaction temperature from 100 °C to room temperature to reach the same experimental conditions as those corresponding to Fig. 10. The corresponding behavior, illustrated in Fig. 14, shows that the initial state of the catalyst before heating at 100 °C could be restored no more unless a calcination treatment at 420 °C was made. Indeed, the results obtained after 1 h of calcination at 420 °C, represented in Fig. 14, show that the initial photocatalytic activity at room temperature can be restored after this oxidation treatment.

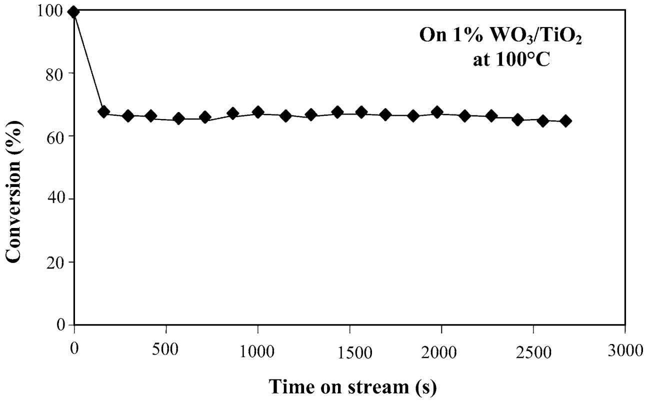


Fig. 13. Evolution of the total conversion (%) for the photooxidation of 500 ppm butyl acetate on 1% WO_3/TiO_2 at 100 °C (50% humidity) versus time on stream (s).

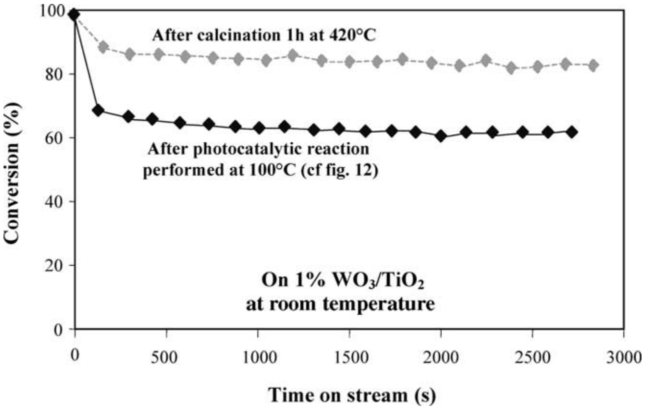


Fig. 14. Evolution of the total conversion (%) for the photooxidation of 500 ppm butyl acetate on 1% WO_3/TiO_2 at room temperature (50% humidity) versus time on stream (s).

4. Discussion

4.1. *Influence of the catalyst recovering ratio or coating thickness*

As presented in Section 3.1, the first way to improve photocatalytic activity of TiO_2-based catalysts is to optimize the experimental conditions of the coating thickness on the support. It is known that the UV light intensity decreases with distance to TiO_2 and penetrates only about 4 µm [26,27], so most of the photooxidation takes place in the top part (4 µm) of this layer. This is in contrast with "classical" thermal catalytic oxidation catalysts, if mass transfer is not limited. Another advantage of using a thin layer of catalyst is that, even at relatively low pollutant concentration, it allows steady state to be obtained quickly, because the catalyst encounters many monolayers equivalent of butyl acetate. On the other hand, when the amount of catalyst is increased above a certain thickness, most of the additional catalyst will not be involved in the photooxidation process.

4.2. *Initial decrease of activity*

The general photocatalytic activity and efficiency of TiO_2 seems to be related to both the initial decrease of total conversion and the conversion after reaching the system steady state conditions.

As, under our experimental conditions, the fresh initial surface is not saturated with reactants (butyl acetate and water) before the UV light is switched on, it seems obvious that the first seconds on stream are needed for a surface equilibrium through saturation of reactants. The fact that this initial decay in activity depends on and decreases with water content confirms the assumption of an initial conditioning or equilibrium between water consumption (through OH surface groups) and water formation issued from photocatalytic reaction. That is the reason that, at the very beginning of the reaction, as many of the catalytic sites are unoccupied, the reaction is very efficient (100% conversion), thus leading to a rapid depletion in surface OH groups provided by water. This decrease in OH surface groups should be enhanced as the water content in the reactant feed is low. These assumptions are supported by the diminution of the initial activity decrease when the water content is decreased from 0 to 75%; this difference is more pronounced in the absence of water.

On the other hand, as seen in Fig. 4, an excess ($> 75\%$) of humidity is detrimental for photooxidation, certainly because of the adsorption competition between butyl acetate, oxygen, and water. Although addition of high concentrations of water into the feed might have been expected to displace intermediates from the surface, no different product distributions were obtained in this case.

As demonstrated in this work, the initial decay of photocatalytic activity may be partly due to a surface poisoning with carbonaceous species, which may be initiated by CO_2 as the dominant reaction product. Although it could be supposed that the rate of CO_2 formation and thus the rate of carbonaceous species or poison formation increases with temperature, it seems obvious that these carbonaceous species accumulate on TiO_2 and deactivate it more easily than at room temperature. But, from Fig. 7c, on the contrary, it is observed that CO_2 has significant desorption rate below 200 °C, with a maximum around 150 °C; it can be displaced more readily by water at elevated temperature, thus yielding a less significant poisoning and deactivation effect for a reaction temperature of 100 °C, as confirmed in Fig. 8.

4.3. *Influence of the water content and the reaction temperature on the steady state conditions of the system*

Taking into account the two previous factors responsible for the initial decay in the photocatalytic activity, i.e., the initial conditioning and the poisoning of the surface, an activity at steady state conversion is reached rapidly. Fortunately, under our conditions of a thin coating layer of TiO_2, the steady state is reached quickly (less than 300 s), leading at this point to a conversion at equilibrium and to a very stable photocatalytic activity with no further deactivation. Under these steady state conditions, it can be considered obvious that the photooxidation process is dependent on factors such as relative humidity and reaction temperature.

It has been sparsely reported in the literature that hydroxyl radicals may initiate and are a major participant in various photocatalytic reactions [3,28,29]. These hydroxyl radicals are issued from reactions with the hole being created in the valence band with adsorbed H_2O or OH^- species. Thus, these explanations are in good agreement with the results represented in Fig. 4, showing that the photocatalytic activity is enhanced at steady-state conditions when greater amounts of water were added to the reactant feed. Thus, even without water added to the feed, the water formed during reaction is adsorbed on the surface sufficiently that the photocatalytic processes can proceed but in a less efficient way than under wet conditions.

The effects of the increase of the reaction temperature may be multiple. First, as is known and has been reported previously for some organic reactants [23,30,31], the photooxidation process rate increases with temperature from 25 to about 100 °C. Second, it is evident that an increase of temperature modifies the adsorption–desorption equilibrium between reactants (butyl acetate, oxygen, water) and reaction products (CO_2 and water). It seems likely that adsorption–desorption processes are involved and it can be supposed that at 100 °C these processes are thermally activated.

4.4. *Influence the addition of platinum*

Under our experimental conditions, the addition of 1 to 10% (weight) of Pt to TiO_2 photocatalyst is detrimental at room temperature and at 100 °C. As there was no reaction in the dark, even at 100 °C, Pt is considered inactive for thermal catalytic oxidation. However, and according to some authors [3], addition of Pt or other noble metals to TiO_2 has been found to improve photocatalytic efficiency [23,30] in many photooxidation reactions and mainly in liquid media. In these cases, the increase of photoefficiencies was explained by the Schottky barrier effect at the metal$/TiO_2$ interface, so that electrons could be transported to the noble metal [31], whereas at the same time, holes are accumulated at the Pt/TiO_2 interface leading to a charge carrier separation and thus to a decrease of electron–hole recombination.

Unfortunately, since the Pt/TiO_2 interface is not as developed in the gas phase as in the liquid phase, we suppose that this electron effect does not occur on thermally reduced Pt/TiO_2 catalyst under our experimental conditions. Some other studies on the effect of Pt deposit on TiO_2 [23] have revealed that an electron transfer occurred from TiO_2 to Pt and that it resulted in too much electron enrichment of Pt particles, increasing with the Pt content. Ishitan et al. [23] concluded that there was an optimum Pt content, resulting on the one hand from a compensation between a decrease of electron–hole recombination at the TiO_2 surface and on the other hand to an electron–hole recombination on the Pt particles (in the case of high Pt contents), acting as recombination charge centers.

But, under our experimental conditions, no difference in photocatalytic behavior has been detected between 1 and 10% Pt/TiO_2 catalysts. So, one of the most probable interpretations for the detrimental effect obtained on our Pt/TiO_2 catalyst samples, with metal contents varying from 1 to 10% and with variable reaction temperatures, may be that it is a consequence of the catalyst preparation method. Indeed, Pt/TiO_2 catalysts were prepared by $PtCl_6{}^-$ anion adsorption at low pH values, though the samples were thermally reduced after H_2PtCl_6 impregnation. However, the catalyst was not washed after adsorption of the $PtCl_6{}^-$ anions, as is done usually in "classical impregnation," yielding a longer period of contact between the TiO_2 and the unreduced anionic solution. In our opinion, this could lead to an acidic etching of the TiO_2 surface with probable formation of amorphous TiO_2 layers with a loss of crystallinity, as already shown elsewhere [16] with a HRTEM micrograph. On the other hand, it has already been reported that TiO_2 crystallinity plays an important role in photooxidation reactions.

4.5. *Influence of the addition of WO_3*

Photocatalytic reactions occurring on a semiconductor surface (in general TiO_2) are considered to proceed via the following steps: (1) adsorption of reactants, particularly of the organic pollutant, (2) reaction in the adsorbed phase, (2i) absorption of photons, (2ii) production of electron–hole pairs by band gap excitation, (2iii) space charge separation by traps available on the catalyst's surface, (2iv) redox processes induced by separated electrons and holes with the adsorbates on the surface, and (3) desorption of reaction products.

So, on TiO_2, the photocatalytic activity may be limited mainly by the photocatalytic phenomenon itself through the recombination between the photogenerated charges or by the low abilities for adsorption of some organic compounds and/or desorption of reaction products or carbonaceous poisoning species.

Thus, from the different results obtained on WO_3/TiO_2 catalyst samples, it can be deduced that the beneficial effect of the addition of WO_3 can be summarized as follows.

4.5.1. *Increase of surface acidity*

Many studies dealing with WO_3 deposited on various supports including TiO_2 have demonstrated that WO_3/TiO_2 catalysts exhibit surface acidity issued from the presence of Lewis and Brønsted acidic sites related to W^{6+} species [10]. Thus, the WO_3/TiO_2 acidic surface has an higher affinity for species with unpaired electrons. That is why it may adsorb a greater amount of OH^- or H_2O, which is considered to be necessary for the generation of OH radicals, and enhance the hydrophilic properties of the surface. So, the considerable increase of photocatalytic activity on 1% WO_3/TiO_2, especially in the presence of water, can be explained. At the same time, the catalyst is able to more easily adsorb organic reactants with polarized functional groups having high affinities with acidic surfaces. Nevertheless, it seems obvious that this affinity toward organics should not be too important due to the risk of limiting their degradation by a too strong adsorption.

On the other hand, the increase of surface acidity may prevent the initial deactivation by a better desorption of carbonaceous species, carboxylates, or more probably CO_2, which is known to exhibit a bad affinity with acidic surfaces in the presence of water. These assumptions are confirmed in Figs. 11a and 11b, where it is clearly shown that the initial carbon deficit and decrease of activity is lowered, mainly with increasing water content (Fig. 11b).

4.5.2. Increase of surface acidity—retarding the electron–hole recombination processes

The beneficial effect of WO_3 on photocatalytic activity can be explained by the loading of electron-accepting species on the TiO_2 surface, which is a good way of slowing electron–hole recombination. So, according to some authors [11,21,32] and since W(VI) can be easily reduced in W(V) [11], it can be deduced that the photoexcited electrons in the conduction band of TiO_2 can be easily accepted by WO_3, following the scheme $W^{6+} + e^-_{(TiO2)cb} \rightarrow W^{5+}$. In this case, WO_3 helps in the trapping of photogenerated electrons, thus limiting charge recombination, which is one of the limiting factors in photocatalytic reactions on TiO_2. This has also been confirmed in the literature [10] by charge transfer measurements (using Vis–UV diffuse reflectance spectroscopy) of photoproduced electrons from TiO_2 to W^{6+}; this charge transfer increased as the WO_3 content increased.

But, on the other hand, it must be taken into account that too-high-loaded WO_3/TiO_2 catalysts could act as recombination centers for electron–h^+ pairs, according to the scheme $W^{6+} + e^-_{(TiO2)\,cb} \rightarrow W^{5+}$ but $W^{5+} + h^+_{(TiO2)vb} \rightarrow W^{6+}$. So, as observed and confirmed in this paper, an optimum in WO_3 content is necessary to optimize its role of photogenerated electron trapping.

In our studies it can be supposed that the presence of W^{6+} as electron traps is in fact one of the most important factors involved in the enhancement of photocatalytic activity. This is confirmed in Figs. 12 and 13, where it is observed that the increase of reaction temperature from room temperature to 100 °C in wet feeds is detrimental for the total activity, certainly because of reduction of a part of W^{6+} in lower oxidation states. Furthermore, after this test at 100 °C, a decrease of reaction temperature to room temperature does not restore the initial activity except after calcination in dry air at 420 °C, which results in reoxidation in W^{6+} surface species (Fig. 14).

4.5.3. Increase of surface acidity—semiconductor properties of WO_3

Since WO_3 is known as a semiconductor with a band gap of 3.0 eV and with valence and conduction band potentials slightly more cathodic than those of TiO_2, these semiconductor properties should be considered. But, in our experiments, since increasing the loading of WO_3 beyond 4%, which is the optimal content, to 10% results in photoactivity decreases, it can also be supposed that WO_3 itself is insufficient as photocatalyst. Nevertheless, it can be deduced that the coupling of two semiconductors with comparable band gaps and with conduction and valence bands suitably disposed can lead to a simultaneous electron transfer between the coupled semiconductors [18,33]. But, according to some authors [33], the improvement of photooxidation in the case of coupled semiconductors may be partly due to intimate contact between the two semiconductors, which was certainly not the case with our preparation method.

5. Conclusions

The photocatalytic efficiency of TiO_2 can be greatly improved via chemical and electronic modifications. The addition of Pt in various contents leads to disappointing results. However, the associated WO_3 and TiO_2 systems, after optimization of the tungsten oxide content, allowed significantly higher photoactivity than the pure TiO_2 photocatalyst. This enhanced photocatalytic efficiency has been attributed mainly to the presence of a surface acidity, to the presence of electron-trapping centers (W^{6+}), and, in a less important manner, to the intrinsic semiconductor properties of WO_3 which could lead to a coupled semiconductor system.

References

[1] D.F. Ollis, E. Pelizzetti, N. Serpone, Environ. Sci. Technol. 25 (1991) 1522.
[2] R.W. Matthews, J. Phys. Chem. 91 (1987) 3328.
[3] D.F. Ollis, E. Pelizzetti, N. Serpone, in: N. Serpone, E. Pelizzetti (Eds.), Photocatalysis: Fundamentals and Applications, Wiley, New York, 1989, pp. 604–637.
[4] R.M. Nimlos, W.A. Jacoby, D.M. Blake, T.A. Milne, Environ. Sci. Technol. 27 (1993) 732.
[5] J. Fan, J.T. Yates Jr., J. Am. Chem. Soc. 118 (1996) 4686.
[6] N. Djeghri, S. Teichner, J. Catal. 62 (1980) 99.
[7] R. Bickley, G. Munuera, F.S. Stone, J. Catal. 31 (1973) 398.
[8] J. Cunningham, B. Hodnett, J. Chem. Soc. Faraday Trans. 1 77 (1981) 277.
[9] Y. Ohko, K. Hashimoto, A. Fujishima, J. Phys. Chem. A 101 (1997) 8057.
[10] C. Martin, L. Palmisano, V. Rives, A. Sclafani, Catal. Lett. 49 (1997) 235.
[11] K. Tennakone, O.A. Heperuma, J.M.S. Bandara, W.C.B. Kiridena, Semicond. Sci. Technol. 7 (1992) 423.
[12] D. Robert, A. Piscoro, O. Heintz, J.V. Weber, Catal. Today 54 (1999) 291.
[13] A. Fernandez, G. Lassaletta, V.M. Jimenez, A. Justo, A.R. Elipe-Gonzalez, J.M. Herrmann, H. Tahiri, Y. Ait-Ichou, Appl. Catal. B. Environmental 7 (1995) 49.
[14] J.M. Herrmann, J. Matos, J. Disdier, C. Guillard, J. Laine, S. Malato, J. Blanco, Catal. Today 54 (1999) 255.
[15] K.J. Green, R.J. Rudham, Chem. Soc. Faraday Trans. 89 (1993) 1867.
[16] J.C. Kennedy, A.K. Datye, J. Catal. 179 (1998) 375.
[17] Y.C. Liu, G.L. Griffin, S.S. Chan, I.E. Wachs, J. Catal. 94 (1985) 108.
[18] N. Serpone, P. Maruthamuthu, P. Pichat, E. Pelizzeti, H. Hidaka, J. Photochem. Photobiol. A. Chemistry 85 (1995) 247.
[19] W. Lee, Y.R. Do, K. Dwight, A. Wold, J. Solid State Chem. 108 (1994) 198.
[20] W. Lee, W.M. Gao, K. Dwight, A. Wold, Mater. Res. Bull. 27 (1992) 685.
[21] Y.R. Do, W. Lee, K. Dwight, A. Wold, J. Solid State Chem. 108 (1994) 198.
[22] Y.T. Kwon, K.Y. Song, W.I. Lee, G.J. Choi, Y.R. Do, J. Catal. 191 (2000) 192.

[23] O. Ishitani, C. Inoue, Y. Suzuki, T. Ibusuki, J. Photochem. Photobiol. A. Chem. 72 (1993) 269.
[24] J.L. Falconer, K.A. Magrini-Bair, J. Catal. 179 (1998) 171.
[25] H. Courbon, J.M. Herrmann, P. Pichat, J. Phys. Chem. 88 (1984) 5210.
[26] M. Formenti, F. Juillet, P. Moriaudeau, S. Teichner, J. Chem. Tech. 1 (1971) 680.
[27] W.A. Jacoby, D.M. Blake, R.D. Noble, C.A. Koval, J. Catal. 157 (1995) 87.
[28] H. Gerischer, A. Heller, J. Phys. Chem. 95 (1991) 5262.
[29] C. Turchi, D.F. Ollis, J. Catal. 122 (1990) 178.
[30] P. Pichat, J.M. Herrmann, J. Disidier, H. Coubon, M.N. Mozzanega, Nouv. J. Chim. 5 (1993) 627.
[31] J. Disdier, J.M. Herrmann, P. Pichat, J. Chem. Soc. Faraday Trans. 1 79 (1983) 651.
[32] G. Marci, L. Palmisano, A. Sclafani, A.M. Venezia, R. Campostini, G. Carturan, C. Martin, V. Rives, G. Solana, J. Chem. Soc. Faraday Trans. 92 (1996) 819.
[33] A. Di Paola, L. Palmisano, V. Augugliaro, Catal. Today 58 (2000) 141.