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Catalysis Today 53 (1999) 695–702

CATALYSIS TODAY

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The role of H_2O in the photocatalytic oxidation of toluene in vapour phase on anatase TiO_2 catalyst
A FTIR study

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Abstract

Photocatalytic oxidation of toluene has been carried out in a gas–solid regime by using polycrystalline anatase TiO_2 in a fixed-bed continuous reactor. Air containing toluene and water vapours in various molar ratios was fed to the photoreactor irradiated by a medium pressure Hg lamp. Toluene was mainly photo-oxidised to benzaldehyde, and small amount of benzene, benzyl alcohol and traces of benzoic acid and phenol were also detected. In the presence of water, no decrease of photoreactivity was observed at steady-state conditions. By removing water vapour from the feed, the conversion of toluene to benzaldehyde was almost completely inhibited, and an irreversible deactivation of the catalyst occurred. FTIR investigations indicated that benzaldehyde is photoproduced on the TiO_2 surface even in the absence of water vapour, but exposure of the catalyst to the UV light in a dry atmosphere results in an irreversible consumption of surface hydroxyl groups. As these species play a key role in the photoreactive process, this dehydroxylation should be the reason of the catalyst deactivation observed in the catalytic runs carried out in the absence of water vapour. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous photocatalysis; TiO_2; Toluene photo-oxidation

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1. Introduction

Volatile organic compounds, VOCs, are an important class of pollutants usually found in the atmosphere of all urban and industrial areas. Toluene is one of these compounds and, due to its noxious nature, several strategies have been adopted in order to reduce its presence in indoor and industrial emissions. Among various methods which are effective in oxidising toluene, heterogeneous photocatalysis is one of the most attractive, as it can be successfully carried out in mild conditions. For this reason, photocatalysis has been largely employed for the oxidation of many organic compounds in the liquid–solid regime [1–3], while a few cases of photoreactions in the gas–solid regime are reported [4–11].

Nevertheless, it is worth noting that an exhaustive description of the mechanism of reaction is very important in the photo-oxidative degradation of VOCs, in order to know if product(s) more dangerous than the starting substrate is(are) produced and to design photoreactors suitable to achieve complete mineralisation.

As the gas–solid regime is concerned, Ibusuki and Takeuchi [12] reported experiments of photo-oxidation

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PII: S0920-5861(99)00156-X

of toluene on TiO_2 in the presence of water vapour carried out at room temperature. They used four photoreactors in series and they found that the presence of water was beneficial in order to achieve the almost complete photo-oxidation of toluene, benzaldehyde having been detected only in very small amounts.

Moreover, Obee and Brown [13] studied the photo-oxidation of toluene and other organic pollutants in gas–solid regime by using polycrystalline TiO_2 as catalyst, and, in particular, the influence on the photo-oxidation rate of the competitive adsorption between water and toluene vapours was investigated.

In a previous paper, we reported a combined catalytic and FT–IR study of the partial photo-oxidation of toluene to benzaldehyde in gas–solid regime by using polycrystalline anatase TiO_2 as catalyst [14]. In that case, we observed that the photocatalytic behaviour was strongly influenced by the presence of water vapour in the gaseous reaction inlet. In fact, benzaldehyde photoproduction achieved steady-state conditions in the presence of water vapour, whereas an almost complete and irreversible depletion of the toluene conversion was obtained by removing water from the feed.

In the present study, we investigated more deeply the phenomena occurring during the photo-oxidation process on the surface of the semiconductor particles by FT–IR spectroscopy, focusing on the nature of surface active species and on their evolution under UV irradiation in wet or dry atmosphere.

2. Experimental

Photo-oxidation runs were carried out by using an anatase TiO_2 powder (Merck, BET specific surface area $10\,m^2\,g^{-1}$) as catalyst. The reactant mixture was generated by bubbling air at atmospheric pressure through saturators containing doubly distilled water and toluene (Carlo–Erba, RS) at room temperature (r.t.). The gas flow rate was $0.42\,cm^3\,s^{-1}$ and the toluene molar fraction was 1.3×10^{-2}. The water molar fraction was held constant to 2.5×10^{-2} in the catalytic tests carried out with a wet gaseous inlet. In a second set of experiments, the same water molar fraction was kept until steady-state condition of toluene fractional conversion to benzaldehyde was attained. After that, water was removed from the inlet gaseous mixture. The photocatalytic experiments were carried out in a flow apparatus using a Pyrex fixed-bed cylindrical reactor, whose dimensions were internal diameter 1 cm, external diameter 1.2 cm, and height 30 cm. The reactor was vertically mounted inside a chamber thermostatted at 413 K and a circular aperture made on a wall of the chamber and closed by a sheet of Pyrex glass (0.3 cm thick) allowed its illumination. A 400 W medium pressure Hg lamp (model Polymer GN ZS, Helios Italquartz) was used to irradiate the photoreactor.

For the IR measurements, the TiO_2 powder was pressed in form of self-supporting pellets ($40\,mg\,cm^{-2}$), and then placed in a IR quartz cell, equipped with KBr windows, connected to a conventional vacuum line (residual pressure: 1×10^{-6} Torr; 1 Torr = 133.33 Pa) allowing all thermal treatments and adsorption–desorption experiments to be carried out in situ.

IR spectra ($4\,cm^{-1}$ resolution) were recorded with a Bruker IFS 48 spectrometer.

In the photo-oxidation experiments the pellets were irradiated through the quarts walls of the IR cell by the same type of lamp employed for the catalytic tests, equipped with a pyrex filter. Toluene, H_2O and O_2 (total pressure: 110 Torr) in molar ratios similar to those in the feed of the photoreactor were admitted onto the samples during the irradiation.

High purity O_2 (Matheson) was employed without any further purification except liquid nitrogen trapping, while H_2O and toluene were admitted onto the samples after several freeze–pump–thaw cycles.

3. Results and discussion

3.1. Effect of H_2O on the conversion of toluene to benzaldehyde

As previously reported [14], the UV irradiation of the toluene/water/air mixture in the presence of TiO_2 mainly give rises to the production of benzaldehyde. Small amounts of benzene, CO_2, benzyl alcohol and traces of benzoic acid are also produced. After an initial transient period, steady-state conversion of toluene to benzaldehyde was achieved after 70 h of irradiation. The run then lasted for 350 h and no decrease of

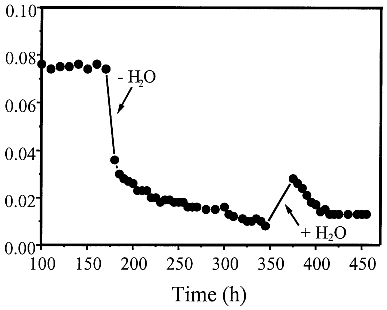

Fig. 1. Effect of the removal of water from the inlet gaseous mixture on the toluene fractional conversion to benzaldehyde starting by the steady-state condition of the reaction (fractional conversion = 0.08) and the subsequent re-introduction of the water vapour.

the benzaldehyde photoproduction was observed. In a second set of experiments, water was eliminated from the inlet gaseous mixture starting from the steady-state condition of the reaction. As shown in Fig. 1, the toluene fractional conversion to benzaldehyde is reduced by 50% after few hours of reaction in dry conditions, and then it decreases to very low values over longer time of reaction. A subsequent readmission of water in the reaction mixture leads only to an initial and partial recovery of the activity, which then turns down to a level very close to that observed before in the absence of water.

This behaviour indicates that water vapour is needed to keep steady-state toluene conversion to benzaldehyde, and that in the presence of a dry toluene/air reaction mixture an irreversible deactivation of the catalyst occurs.

3.2. FT–IR studies

To investigate the phenomena occurring onto the surface of the catalyst during the reaction process in both hydrated and dry conditions, toluene photo-oxidation in the presence and in the absence of H_2O was studied by FT–IR spectroscopy. In these experiments the IR cell was used as a ‘batch reactor’, by admitting a due amount of reaction mixture onto the catalyst and then exposing the system to the UV light through the quartz walls of the cell. The toluene/H_2O/O_2 or toluene/O_2 mixtures were admitted onto the catalyst pre-outgassed at room temperature, a full monolayer of hydroxyl groups and water molecules still covering the surface of the TiO_2 microcrystals after this treatment [13–18]. This condition was assumed as an acceptable model of the surface hydration of the TiO_2 powder during the photocatalytic test when water vapour was present in the inlet gaseous feed.

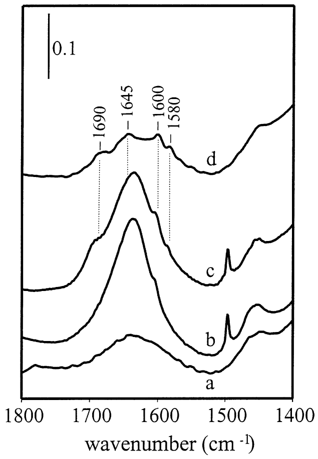

Fig. 2. Photo-oxidation of toluene on TiO_2 catalyst in the presence of water vapour and O_2. IR spectra (1800–1400 cm^{-1} range) of the TiO_2 catalyst: (a) after outgassing at room temperature (r.t.) for 45 min; (b) in the presence of the toluene/H_2O/O_2 mixture (3 : 7 : 100 Torr); (c) after exposure to the UV light for 10 min; (d) after subsequent outgassing at r.t. for 45 min.

Fig. 2 reports the IR spectra obtained in the case of the toluene adsorption and photo-oxidation in the presence of water vapour. In the 1800–1400 cm^{-1} range the spectrum of the catalyst outgassed at r.t. exhibits a broad band at ca. 1640 cm^{-1} due to water molecule coordinated to surface Ti^{4+} cations [13–18] and a component at 1455 cm^{-1} assignable to carbonate-like groups, produced by reaction of CO_2 with basic centres on the TiO_2 surface during the storage of the catalyst powder in air (Fig. 2(a)).

After admission of the toluene/H_2O/O_2 mixture the spectrum of the sample appears dominated by a peak at 1635 cm^{-1} due to physisorbed water, and weaker bands due to aromatic molecules are present at 1600, 1496 and 1460 cm^{-1} (Fig. 2(b)).

By exposing the system to the UV light for 10 min a slight decrease of the 1496 and 1460 cm^{-1} bands is observed, while new weak components appear at 1690, 1645 (shoulder of the main δ_{H_2O} absorption at 1635 cm^{-1}), and 1580 cm^{-1}, and a slight increase in intensity of the 1600 cm^{-1} band occurs (Fig. 2(c)).

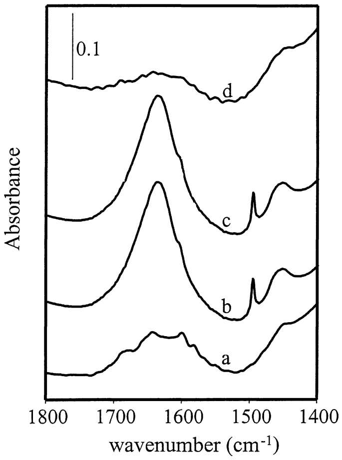

Fig. 3. IR spectra (1800–1400 cm^{-1} range) of the TiO_2 catalyst: (a) in the presence of adsorbed benzaldehyde produced by the photo-oxidation of toluene (the same as curve d in Fig. 2); (b) after the admission of H_2O and O_2 (7 : 100 Torr); (c) after exposure to the UV light for 10 min; (d) after subsequent outgassing at r.t. for 45 min.

A subsequent outgassing at room temperature completely removes the absorptions due to physisorbed water molecules and unreacted toluene, while bands at 1690, 1645, 1600 and 1580 cm^{-1} due to the newly formed species are left (Fig. 2(d)). As previously reported, these components are due to irreversibly adsorbed benzaldehyde produced by the partial photo-oxidation of toluene [14].

After this stage, H_2O and O_2 were re-admitted onto the catalyst, and the weak features of adsorbed benzaldehyde were completely covered by the intense band due to physisorbed H_2O molecules (Fig. 3(a) and (b)). The sample was exposed to the UV light for 10 min further, but no relevant changes in the IR spectrum were observed (Fig. 3(c)). The band due to physisorbed H_2O molecules disappeared by briefly outgassing, and only the weak and broad band at 1640 cm^{-1} due to molecular water coordinated to surface Ti^{4+} was left (Fig. 3(d)). Noticeably, bands due to adsorbed benzaldehyde appeared strongly reduced in intensity (Fig. 3(d)), indicating that it underwent a transformation under UV irradiation in the presence of H_2O and O_2, while no bands due to newly formed species are observed in the spectrum. This behaviour could be rationalised as follows: in the presence of water vapour the bands due to the species derived from the benzaldehyde reaction cannot be observed owing to the presence of the dominant peak due to physisorbed water (Fig. 3(c)); water and products of the benzaldehyde transformation are then desorbed from the catalyst by outgassing at room temperature (Fig. 3(d)). In the catalytic runs, benzene and CO_2 were detected among the products of the photoreaction, resulting from the photodecarboxylation of benzoic acid produced by oxidation of benzaldehyde [14]. It can be supposed that the same reactions occurred in the model conditions employed in the IR cell, yielding the consumption of adsorbed benzaldehyde to form benzoic acid and then CO_2 and benzene. Parallel experiments evidenced that this last species is physisorbed on TiO_2 weakly, and it is completely desorbed from the catalyst by outgassing at room temperature. As previously reported, carbonate groups are present on the fresh catalyst (see Fig. 2(a)), due to the reaction of surface basic sites with CO_2 during the storage of the TiO_2 powder in air. As a consequence, no basic centres should be available on the catalyst surface to fix further CO_2 molecules derived from the decarboxylation of benzoic acid produced by the photo-oxidation of adsorbed benzaldehyde.

In conclusion, both CO_2 and benzene, if formed, should be desorbed from the catalyst during the outgassing subsequent to the UV irradiation.

Insights on the behaviour of the surface species of the TiO_2 powder during the photo-oxidation process were obtained by analysing the high frequency region of the spectrum of the catalyst, where the absorptions due to the stretches of hydroxyl groups and adsorbed water molecules are observed. The reaction mechanism previously proposed [14] assigns a relevant role in the photo-oxidation process to radical $^{\bullet}OH$ species generated by interaction of the photogenerated holes, h^+, with surface hydroxyl groups. These radical species can extract a hydrogen atom from the methyl groups of adsorbed toluene molecules, which is the first step of the oxidative process yielding benzaldehyde. Surface –OH groups are restored during the process by reactions involving adsorbed oxygen and water molecules. After simply outgassing at r.t. the spectrum of the catalyst exhibits an asymmetric peak at 3665 cm^{-1}, due to the stretching mode of free hydroxyl groups, and a broad band at 3600–3250 cm^{-1}, resulting from the overlap of the bands due to the

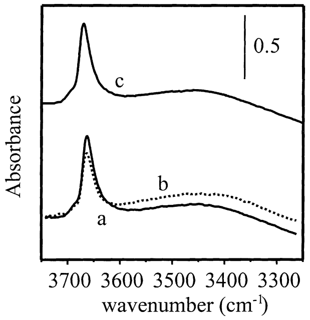

Fig. 4. IR spectra of the TiO_2 catalyst, in the 3750–3250 cm^{-1} range, at the different stages of the photo-oxidation of toluene in the presence of H_2O vapour and O_2: (a) after outgassing at r.t. for 45 min; (b) after admission of the toluene/H_2O/O_2 mixture, exposure to the UV light for 10 min and subsequent outgassing at r.t. for 45 min; (c) after admission of H_2O and O_2, exposure to the UV light for 10 min and subsequent outgassing at r.t. for 45 min. Intermediate spectra of the catalyst in the presence of the reaction mixture are not shown, as in those cases only the very intense band due to the stretches of adsorbed H_2O molecules is present.

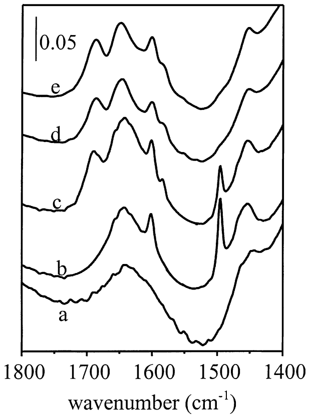

Fig. 5. Photo-oxidation of toluene on the TiO_2 in the presence of O_2 only. IR spectra (1800–1400 cm^{-1} range) of the TiO_2 catalyst: (a) after outgassing at room temperature for 45 min; (b) in the presence of the toluene/O_2 mixture (3 : 100 Torr); (c) after exposure to the UV light for 10 min, (d) after subsequent outgassing at r.t. for 45 min; (e) after 10 h UV irradiation in the presence of O_2 (100 Torr).

stretching modes of hydrogen bonded –OH groups and of water molecules co-ordinated to surface Ti^{4+} cations (Fig. 4(a)) [13–18].

As reported above, the catalyst was contacted with the toluene/H_2O/O_2 mixture and exposed to the UV light, resulting in the production of benzaldehyde on the catalyst surface. After outgassing at r.t. to remove physisorbed water molecules and unreacted toluene, the band at 3665 cm^{-1} appeared slightly decreased in intensity, while a slight increase in intensity of the 3600–3250 cm^{-1} absorption is observed (Fig. 4(b)). This behaviour suggests that free hydroxyl groups, other than as source of $^{\bullet}OH$ radical, act as adsorption sites for benzaldehyde, their absorption frequency being shifted to lower frequency by the interaction with photoproduced molecules. The original intensity of the band at 3665 cm^{-1} appeared almost restored in the spectrum of the catalyst submitted to a subsequent UV irradiation in the presence of water vapour and oxygen and finally outgassed at r.t. (Fig. 4(c)), this treatment resulting in a removal of benzaldehyde molecules from the catalyst surface (see Fig. 3(d)). Noticeably, subsequent UV irradiation of the catalyst in the presence of H_2O and O_2 did not produce any decrease in intensity of the peak at 3665 cm^{-1}, even after 10 h exposure to the UV light (spectrum not reported). This indicates that the amount of surface hydroxyl groups, which are the source of radical species active in the photo-oxidative process, is not significantly modified by UV irradiation in a wet atmosphere.

In a second experiment, the catalyst pre-outgassed at r.t. (Fig. 5(a)) was contacted with O_2 and toluene only, and the features of the adsorbed organic molecules are clearly observed at 1600, 1496 and 1460 cm^{-1} (Fig. 5(b)). After 10 min exposure to the UV light a decrease in the toluene bands was observed, and absorptions related to photoproduced benzaldehyde appeared at 1690, 1645, 1600 and 1580 cm^{-1} (Fig. 5(c)). The bands due to this newly formed species are more clearly distinguishable in the spectrum recorded after outgassing at r.t. the unreacted toluene (Fig. 5(d)). This behaviour clearly indicates that benzaldehyde is photoproduced on the catalyst surface even in the absence of water vapour in the reaction mixture.

Oxygen was then re-admitted into the cell, and the sample was UV irradiated for increasing time. No relevant modifications in the spectral features of adsorbed benzaldehyde were observed, even after 10 h exposure to the UV light (Fig. 5(e)). It can be then inferred that the further photo-oxidation of this species (i.e. to form benzoic acid and then CO_2 and benzene) is strongly inhibited in the absence of water vapour.

In contrast, the inspection of the high frequency range of the spectra evidenced a significant evolution

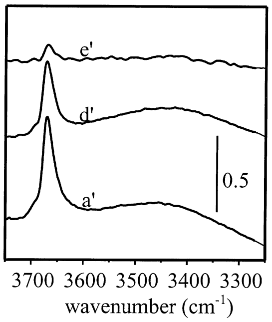

Fig. 6. IR spectra of the TiO_2 catalyst, in the 3250–3750 cm^{-1} range, at the different stages of the photo-oxidation of toluene in the presence of O_2. Curves a′–e′ as curves a–e in Fig. 5. Spectra b′ and c′ are not shown, as in the presence of physisorbed toluene the 3665 cm^{-1} peak is not present, being transformed into a broad and complex absorption located at lower frequency [14].

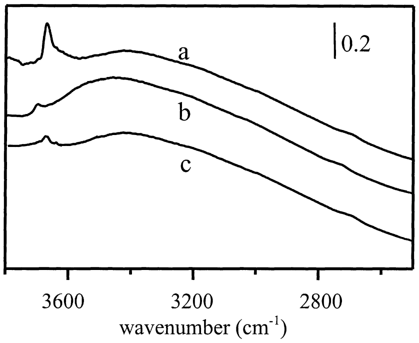

Fig. 7. Effect of the exposure to the UV light on the surface hydration of the TiO_2 catalyst. IR spectra of the catalyst : (a) after outgassing at r.t. for 45 min; (b) after exposure to the UV light for 10 min in the presence of 100 Torr dry O_2; (c) after outgassing at r.t. for 45 min.

of the ν_{OH} band under these conditions. As observed in the previous set of experiment (see Fig. 4), the band at 3665 cm^{-1} is slightly decreased in intensity by the production of benzaldehyde on the catalyst surface (Fig. 6(a′) and (d′)). Subsequent UV irradiation of the sample in the presence of O_2 resulted in a progressive erosion of the hydroxyl peak, the intensity of which appeared strongly reduced after 10 h exposure to the UV light (Fig. 6(e′)). Noticeably, the readmission of water onto the such irradiated catalyst did not yield in a recovery in intensity of the 3665 cm^{-1} band, neither in the dark nor after UV irradiation (spectra not reported). This indicates that an irreversible dehydroxylation of the catalyst surface occurred during the exposure to the UV light in O_2.

It is worth noting that this dehydroxylation cannot be due to consumption of –OH groups in oxidative process involving organic molecules, as neither toluene was present during the irradiation nor adsorbed benzaldehyde underwent a further oxidation.

To further investigate this behaviour a parallel experiments was carried out by exposing the TiO_2 powder to the UV light in dry oxygen. As previously commented on, the spectrum of the catalyst simply outgassed at r.t. exhibits the peak at 3665 cm^{-1} and the broad band at 3500–2800 cm^{-1}, due to free hydroxyl groups and molecular water coordinated to Ti^{4+} cations, respectively (Fig. 7(a)). After exposure to the UV light for 12 h in dry O_2 these features was replaced by an intense absorption at 3500–2800 cm^{-1}, with a weaker peak at 3690 cm^{-1}, characteristic of water molecules physisorbed onto the catalyst (Fig. 7(b)) [18]. A subsequent outgassing at r.t. removed these species from the surface, and the bands due to free hydroxyl groups and molecular water coordinated to Ti^{4+} cations were observed again. Noticeably, the peak at 3665 cm^{-1} appeared strongly reduced in intensity, indicating that hydroxyl groups were consumed under UV irradiation. Likely, this process might occur through the formation of hydrogen peroxide by coupling of photogenerated $^{\bullet}OH$ radicals, which then decomposes in H_2O and O_2. Oxygen molecules are released in the gas phase, while water molecule are physisorbed onto the catalyst surface (Fig. 7(b)).

As a subsequent step, the toluene/H_2O/O_2 mixture was admitted onto the sample dehydroxylated by exposure to the UV light in dry oxygen (Fig. 8(a)). Also, in this case, the admission of the reactants onto the catalyst produces bands due to physisorbed H_2O and toluene molecules (Fig. 8(b)). Furthermore, the intensity of such bands is quite similar to that observed in the case of the fully hydrated sample under equivalent pressure of reaction mixture (Fig. 2 (a) and (b)), and this suggests that the amount of adsorbed species in the two cases is comparable.

Nevertheless, after 10 min of UV irradiation no significant changes in the spectral profile are observed (Fig. 8(c)), and after outgassing the reaction mixture at r.t. only traces of bands due to photoproduced benzaldehyde are hardly recognisable in the spectrum (Fig. 8(d)).

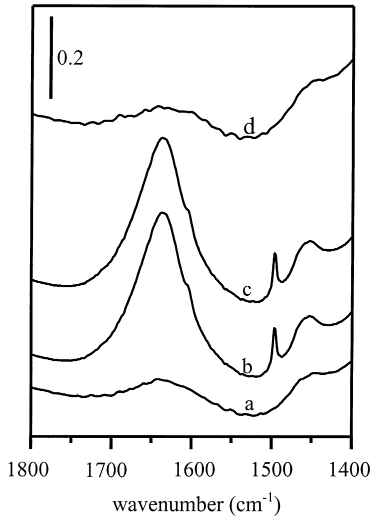

Fig. 8. Photo-oxidation of toluene on the TiO_2 catalyst previously dehydroxylated by UV irradiation in dry O_2. IR spectra of the catalyst: (a) after exposure to the UV light for 10 min and subsequent outgassing at r.t. for 45 min (the same treatment as for curve c in Fig. 7); (b) after admission of the toluene/H_2O/O_2 mixture (3 : 7 : 100 Torr); (c) after exposure to the UV light for 10 min; (d) after subsequent outgassing at r.t. for 45 min.

The photo-activity of the TiO_2 sample dehydroxylated under UV irradiation appears strongly reduced with respect to the original hydroxylated catalyst. Also, a loss in activity was observed for a catalyst dehydroxylated by outgassing at 873 K [14]. Both results strongly suggest that the photo-activity in toluene conversion is related to the presence of surface –OH groups. It can be proposed that the irreversible loss of activity occurring in the photocatalytic test after removal of water vapour from the reaction inlet (Fig. 1) could be mainly due to dehydroxylation of the catalyst under UV irradiation in dry conditions.

Furthermore, the results reported above indicate that toluene is photo-oxidised to benzaldehyde on a hydroxylated TiO_2 catalyst even in the absence of water vapour, and that these photoproduced molecules are not further oxidised under prolonged UV irradiation in the presence of O_2 (see Fig. 5). Benzaldehyde could be then produced in the first period after the removal of H_2O vapour from the reactant inlet, when –OH groups are still present on the TiO_2 surface, and accumulated on the catalyst surface. The readmission of water vapour in the gaseous inlet could induce the desorption of a fraction of these molecules, and this may be the origin of the increase of toluene fractional conversion to benzaldehyde obtained soon after the re-introduction of water in the reaction mixture (Fig. 1).

4. Conclusions

In the adopted gas–solid regime, the photo-oxidation of toluene to benzaldehyde on TiO_2 powder attains steady-state conditions in the presence of water vapour in the gaseous inlet. A progressive and irreversibly decrease of the photoreactivity down to negligible values is observed by removing water from the feed.

FT–IR experiments carried out in model conditions indicate that the layer of surface –OH groups is kept essentially unchanged under UV irradiation in the presence of H_2O vapour, whereas it is irreversibly depleted by exposure to the UV light in dry conditions. As surface hydroxyls are needed to photo-oxidise toluene to benzaldehyde, this may be the origin of the almost complete and irreversible depletion of the toluene conversion by using a dry reaction mixture.

Furthermore, the results indicated that photoproduced benzaldehyde can undergo a further photo-oxidation in the presence of water vapour, whereas this species is essentially unaffected under UV irradiation in dry O_2.

Acknowledgements

The authors acknowledge the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Rome) for financial support.

References

[1] Schiavello (Ed.), Photocatalysis and Environment, Trends and applications, Kluwer, Dordrecht, 1988.
[2] Pelizzetti, N. Serpone (Eds.), Photocatalysis, Fundamentals and Applications, Wiley, New York, 1989.
[3] F. Ollis, H. Al-Ekabi, (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier Science Publisher, New York, 1993.
[4] V. Augugliaro, L. Palmisano, M. Schiavello, A. Sclafani, J. Catal. 99 (1986) 62.
[5] A. Sclafani, L. Palmisano, M. Schiavello, V. Augugliaro, S. Coluccia, L. Marchese, New J. Chem. 12 (1988) 129.

[6] L. Palmisano, A. Sclafani, M. Schiavello, V. Augugliaro, S. Coluccia, L. Marchese, New J. Chem. 12 (1988) 137.
[7] L. Palmisano, M. Schiavello, A. Sclafani, S. Coluccia, L. Marchese, New J. Chem. 12 (1988) 847.
[8] L.A. Dibble, G.B. Raupp, Environ. Sci. Technol. 26 (1992) 492.
[9] M.R. Nimlos, W.A. Jacoby, D.M. Blake, T.A. Milne, Environ. Sci. Technol. 27 (1993) 732.
[10] W.H. Glaze, J.F. Kenneke, J. L Ferry, Environ. Sci. Technol. 27 (1993) 177.
[11] J. Fan, J.T. Yates Jr., J. Am. Chem. Soc. 118 (1996) 4686.
[12] T. Ibusuki, K. Takeuchi, Atmos. Environ. 20 (1986) 171.
[13] T.N. Obee, R.T. Brown, Environ. Sci. Technol. 29 (1995) 1223.
[14] V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra, L. Palmisano, M. Schiavello, Appl. Catal. B: Environ. 20 (1999) 15.
[15] D.M. Griffiths, C.H. Rochester, J. Chem. Soc. Faraday Trans. 1 73 (1977) 1510 M.
[16] J. Jaycock, J.C.R. Waldsax, J. Chem. Soc. Faraday Trans. 1 70 (1974) 1501.
[17] G. Munuera, F.S. Stone, Discuss. Faraday Soc. 52 (1971) 205.
[18] C. Morterra, J. Chem. Soc. Faraday Trans. 1 84 (1986) 1617.