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Degradation of air contaminants through the use of photoassisted heterogeneous catalysis: CF$_3$COCl studied as an HCFC derivative

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Abstract

CF$_3$COCl is effectively photooxydized when a gaseous sample interacts with an illuminated TiO$_2$ covered surface.

The oxidation occurs irrespective of the presence of O$_2$. The main products are CO$_2$ and CF$_2$O. It was observed that a poisoning of the catalyst occurred after successive runs and a partial recovery when ambient air entered the cell, thus, pointing to water as the responsible for the recovery. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the last 10 years, great effort has been devoted to find better ways of achieving the degradation of many pollutants. Many laboratories and researchers in the world have themselves concentrated in finding solutions to the environmental threat. In particular, the gas-phase contaminants have played a prime role due to the fact that they are daily produced in highly polluted urban areas with the concomitant threat to human health. Thus, the use of advanced oxidation processes (AOPs) that generally use a light source, an oxidant agent and a catalyst or photocatalyst, have been investigated [1]. Among these processes, one of the more promising is the use of TiO$_2$ as the photocatalyst since it can promote electron–hole pairs after absorption of ground level attainable solar radiation in contrast to the traditional photochemical methods that for many of the pollutants require the use of short-wave UV lamps.

The TiO$_2$-photoassisted heterogeneous catalysis has been applied not only to gas-phase contaminants but also to a great variety of systems. In fact, it has been used in the destruction of viruses, bacteria [2] and cancer cells [3], odor control [4], water dissociation to recover fuels [5,6], etc. With gaseous substances, probably the most studied system has been trichloroethylene (TCE) [7–17], followed by a number of others that include volatile organic compounds

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(VOCs) [18–21], NO_x [22,23], ozone [24], chlorinated hydrocarbons [10,13] and CFC-11 [25]. For the latter system in particular, the results have shown that the effectiveness of the method is far from being useful, and this is perhaps one of the reasons why the study of these chlorofluorocarbon molecules has almost been abandoned. After the replacement of the CFCs for the HCFCs and HFCs, there were only very few studies on the HCFs themselves [26,27] or on their stable tropospheric degradation products. CF_3COCl is one of the stable tropospheric degradation products of CF_3CCl_2H and it is expected that increasing amounts will be released to the atmosphere in the near future.

We have studied the photoassisted heterogeneous degradation of CF_3COCl using a very simple, yet highly reliable technique that allows UV illumination and, simultaneously, the possibility of following the time course of reactant and products using FTIR spectroscopy.

2. Experimental

The photocatalytic reactor was a glass IR cell whose inner surface was coated with a TiO_2 film. TiO_2 Degussa P25 BET 45.6 m^2 g^{-1} was adsorbed from a water suspension and then dried at 500 K. Two KBr windows were glued to the ends and black light lamps surrounded the cell. The reactor was wrapped with aluminum foil to increase the efficiency of the illumination, and it was then permanently placed in the optical path of an FTIR IFS 28 Bruker spectrometer. Commercially available samples of CF_3COCl (PCR Research Chemicals) were distilled in vacuum before use.

Oxygen was condensed by passing O_2 at atmospheric pressure through a trap immersed in liquid air. The condensate was then pumped under vacuum several times and transferred to a glass bulb whilst the trap was immersed in liquid air.

In a typical experiment, 1.5 Torr of CF_3COCl were put into the cell and O_2 was then added up to a pressure of 1 atm. Pressures were measured using two different manometers. For pressures below 20 Torr a Bell and Howell 9384 transducer was employed and a Setra model 205-2 was used to read higher pressures.

Some experiments were also carried out without added O_2 to test whether or not there is a reductive reaction taking place in the system.

Blank experiments were performed using the same reactor prior to the TiO_2 coating.

After the reactants were in the cell, an IR spectrum was taken and this was used as reference for the subtractions performed with the spectra taken at later times. Then, the lamps were turned on typically for 30 min and IR spectra were recorded every 2 min. Finally, the lamps were turned off while continuing with the recording of IR spectra to assess that there are no further reactions [28].

3. Results and discussion

Perfluoroacetylchoride is effectively oxidized when the TiO_2-coated surface is illuminated. The blank experiment carried out with exactly the same experimental setup but without the surface covering showed the inertness of CF_3COCl to the direct absorption of light, as can be anticipated on account of its UV absorption spectrum and the emission spectrum provided by the black lights. The only products found were CF_2O, CO_2 and HCl when O_2 is added, and trace quantities of CO in the absence of O_2.

The IR characteristic bands of the reactant and products used for identification were 1928.3, 1942.9, 1955.7 and 937 cm^{-1} for CF_2O, and 1810, 1274, 1239, 1201, 935 and 749 cm^{-1} for CF_3COCl; the band centered at around 2350 cm^{-1} for CO_2 and that center at 2900 cm^{-1} for HCl.

Fig. 1 shows a timed sequence of three particular moments of the photoassisted decomposition of CF_3COCl in the presence of O_2.
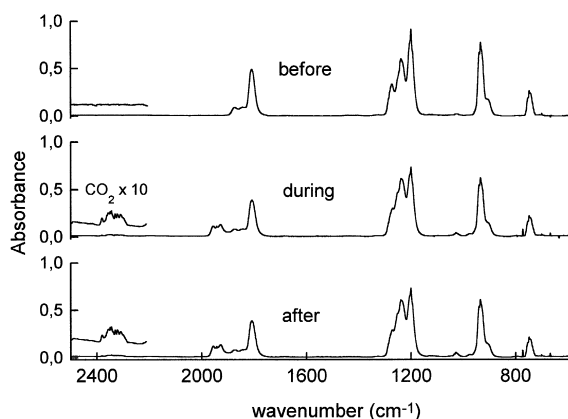
Fig. 1. IR spectra taken from a photocatalytic experimental run. From top to bottom the spectra correspond to: $t = 0$, the last spectrum with the lights on, and the spectrum 15 min after turning the lights off.

The upper trace corresponds to the system before illumination. It is clearly seen that the only species present is the reactant itself and that CO_2 is not present as revealed by the short trace above the spectrum, which is a 10-fold amplification of the spectrum. The middle trace corresponds to the last spectrum taken under illumination (just before turning off the lights). It can be seen there how the reactant bands have decreased and how CF_2O and CO_2 have formed. The CO_2 is again discernible by looking at the amplified trace. The lower trace is a spectrum taken 10 min after turning off the lights. It can be observed that it is essentially the same as the middle one, showing that no further reactions take place with the lights off; a result which is not easily anticipated on account of the results reported in the homogeneous photolysis of CF_3COCl [29].

A similar experiment but carried out in the absence of O_2 would show the same kind of behavior with bigger bands corresponding to the reactant and smaller ones corresponding to the products. This statement can be corroborated in Fig. 2 where the time variation of CF_3COCl concentration has been plotted for these experiments. It can be observed that under the same conditions, up to 50% CF_3COCl can be degraded at around 30 min provided O_2 is present.

In contrast, only a 10% decomposition can be achieved without O_2.

Both experiments show the same oxygenated products. At the pressures used when O_2 is present, the number of collisions assures that there will always be enough oxygen adsorbed on the surface to participate in the reaction. Thus, when no O_2 is present, the system should somehow provide oxygen atoms for the same reaction to take place. The production of oxygen atoms on TiO_2 has often been invoked in the gas–solid heterogeneous photocatalytic oxidation of organics [30]. The sources that could provide oxygen when no O_2 is added should be the oxygen left after the evacuation of the cell itself prior to each experiment (10^{-6} atm), or some other form of active oxygen provided either by the water molecules left after the drying process that upon illumination produce OH [31] and O_2^-, or even by the TiO_2 itself. It is accepted that the first electron transfer products are the oxygen species O_2^- or O^- on the surface [11]. From these arguments, it is reasonable to expect a big difference in the rate at which the oxygen is supplied with and without O_2 added, which justify the results shown in Fig. 2.

Fig. 3 shows another type of experiments performed to probe whether there was a poisoning of the catalyst due to successive experiments. The filled squares correspond to the time course of a run using 1.5 Torr of CF_3COCl in
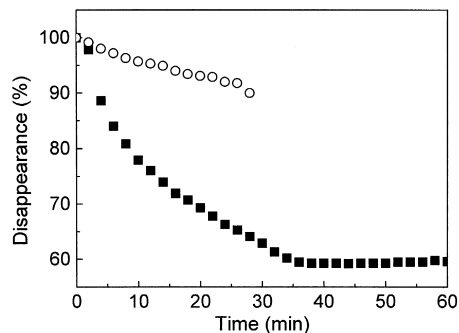

Fig. 2. Time variation of the CF_3COCl concentration for two different experimental conditions. (■) With oxygen added to the system. (○) Without oxygen added.
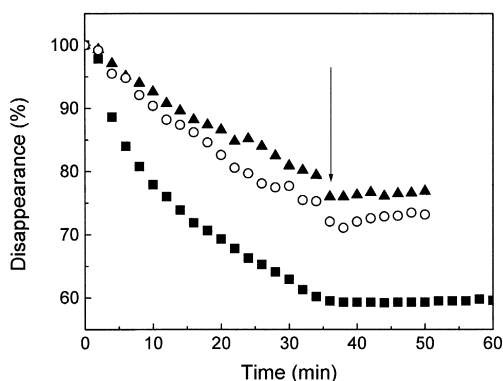
Fig. 3. Time variation of the CF_3COCl concentration when many successive experimental runs are carried out to test the poisoning and subsequent recovery of the catalyst. (■) Freshly prepared TiO_2 surface with oxygen added to the system. (▲) Sixth experiment. (○) Recovery of the surface. Concentrations are taken from the IR spectra at the particular times.

the presence of O_2 for a freshly prepared TiO_2 surface. It can be observed that there is a steep disappearance of reactant with time until the lights are turned off. After this moment (signaled by the vertical arrow on the figure), the concentration remains constant. This indicates the lack of reactions in the absence of light. The solid up-triangles show the results of the sixth experiment carried out in a row, that is, avoiding the possibility of water entering the cell. The system is constructed in such a way that the cell can be evacuated, the reactants loaded at their specific pressures, the photoassisted catalysis performed, and the final products of a typical 1-h experiment discarded, without the need of opening the cell to the air. It is seen that the capability of the catalyst to degrade CF_3-COCl has clearly gone down and only a 20% decomposition is roughly achieved.

Partial recovery of the catalyst surface was observed when the evacuated cell was left closed overnight but detached from the vacuum line. This would allow some ambient air to enter the cell through the small normal valve leaks. The open circles in Fig. 3 show this recovery. Although modest, it is evident that there is a net increase in catalyst activity. To further test this enhancement, other experiments (not shown in

the figure) were conducted where the cell was repeatedly evacuated and opened directly to ambient air, left for 20 min and evacuated again. This procedure amounted to a total of 7–8 times. Finally, the cell was evacuated and the reagents loaded in the usual form. Since the recovery was fairly high, we believe that water molecules could have displaced either CO, CO_2 or CF_2O molecules because of a stronger interaction with the TiO_2. This process has already been postulated by other workers [32] as well as on account of the results for water adsorption that show that the temperatures for desorption are somehow higher than those corresponding to CO and CO_2 [33].

With respect to the products formed in the reaction, it has been already noted that CO forms in trace amounts only when no O_2 is added. Its presence also suggests a fairly weak adsorption on the surface, since our experimental method measures the gas-phase content and not what is adsorbed. When O_2 is added, it is expected that under illumination CO will be oxidized to CO_2 [33–35]. This occurs in our case. The time variation of CO_2 and CF_2O can be seen in Fig. 4. There, it is confirmed that after turning the lights off, there are no further reactions taking place as opposed to what has been reported [32] in the oxidation of some organics where there are intermediate products that remain adsorbed on the surface of the cata-
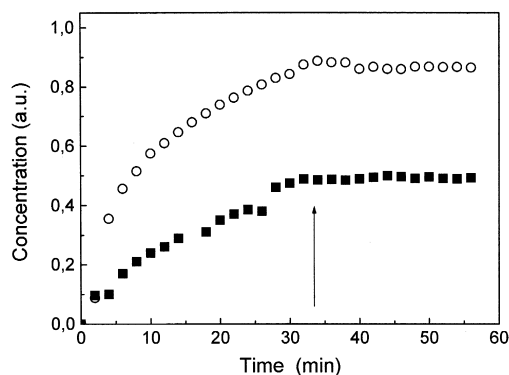

Fig. 4. Time variation in the concentration of the products. Not shown to scale. (○) CF_2O, (■) CO_2.

lyst that promote reactions in the absence of light and in the homogeneous photolysis of CF_3COCl in the presence of O_2 and CO [29]. Another product formed that comes from the Cl atoms produced in the photolysis is HCl. Interestingly, its presence was observed only when the lights were turned off and not during illumination.

From the results presented in this paper, the CF_3COCl degrades by the use of the photoassisted heterogeneous catalysis. This degradation occurs readily without the need of adding other reagents to help the decomposition. For this reason, heterogeneous catalysis is a potential technology to degrade substances such as HCFCs, HFCs and their derivatives, yielding products that do not cause deleterious effects to the ozone layer since the end products are CO_2, CF_2O and HCl or HF. The catalyst is also easily recoverable and this is an advantage when scaling up to treat air masses. Even though this work has been performed in a static system, experiments to transfer it to a flow system are under way.

Acknowledgements

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