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PHOTOCATALYTIC TRANSFORMATION OF C_2Cl_4 IN GAS PHASE UNDER UV-IRRADIATED TITANIUM DIOXIDE

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The photocatalytic transformation of chlorinated solvents has been the topic of numerous works since the first studies of the photocatalytic processes under irradiated semiconductors. A short review will be reported. As an example in the photocatalyzed transformation of perchloroethylene (PCE) in the presence of oxygen the $Cl^{\bullet}$ radical has supposed to have a pivotal role in the first step of the degradation and in the successive transformation of the PCE by-products.[1]. Also in aqueous solution the role of halogen radicals was advanced to explain the formation of CCl_4 from chlorinated methanes.[2]

In this work we investigated the photodegradation of gaseous PCE on titanium dioxide films under UV light at 365 nm at the gas/solid interface. PCE conversion was carried out in a CSTR photo-reactor (Continuous Stirred Tank Reactor) [3] and the residual PCE leaving the reactor was properly detected using a PID detector and FTIR. The C_2Cl_4 photocatalytic transformation was investigated at different experimental conditions, such as at different PCE concentration, TiO_2 irradiated area, inlet gas flow and UV irradiance ($W\cdot m^{-2}$). The water vapor has a detrimental role on the PCE transformation rate due to the competition with PCE adsorption on reactive sites.

The rate and mechanism of transformation change when oxygen is present at high and negligible concentrations. Gaseous products of PCE degradation were determined: CO_2, phosgene, carbon tetrachloride (CCl_4), hexachloroethane (C_2Cl_6) and, at lower concentrations, trichloroacetyl chloride (TCAC) were identified as photodegradation products. In quasi-anoxic conditions significant amount of adsorbed organic compounds with molecular weights higher than that of PCE were produced on the UV-irradiated TiO_2 surface and chloride ions are more accumulated at the surface, proof of the presence of a predominant reductive pathway. However, the addition of chloride ions on TiO_2 surface does not increase the production of gaseous CCl_4.

The production of active chlorine (sum of Cl_2, HClO and $ClO^{\bullet}$) was investigated both in the presence of oxygen and in quasi-anoxic conditions. At low O_2 concentration no gaseous active chlorine was determined, while a significant amount was measured in the presence of oxygen. By considering that in the absence of O_2 the only possible form of active chlorine is Cl_2, the experimental evidences underline that the produced active chlorine is $HClO/ClO^{\bullet}$. Then chlorine radical has a minor role in the abatement of C_2Cl_4.

These experimental data allowed us the identification of the main photodegradation pathways of PCE at high and low oxygen concentration giving intriguing and new insights into the photocatalytic transformation of chlorinated olefins from gaseous phase, putting the role of chloride radicals as reactive species back in a different perspective.

References

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