CARBON CATALYSTS FOR PHOSPHINE ABATEMENT

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Introduction

Abatement of phosphine from crop-storage warehouses is a necessary procedure that must be performed after storage underwent fumigation to deactivate insects. A dual-bed reactor for abatement of phosphine from air in fumigated warehouses was developed by Lorillard Tobacco Company. The process was studied using new modified activated carbon catalysts, as well as the Centaur carbon catalyst from Calgon. A kinetic study of the phosphine abatement process was performed.

Transfer of the abatement system from a process controlled by the gas flow rate provided by the reactor's fan to the process, controlled by internal diffusion of phosphine through the tobacco bales was found. The possibility of the in-situ reactivation of a partially deactivated catalyst by deposition of a small amount of iodine was found. An excessive amount of atmospheric water was found to be a major complication to the long-term use of the carbon-based catalyst. The recirculation of phosphine-containing gas back to warehouse is suggested to keep the catalyst relatively dry and active in oxidation of phosphine and in retaining phosphoric acid, the reaction product.

The study revealed that the overall process involves the initial fast adsorption of phosphine, oxidation of surface compounds and slow diffusion of both phosphine and oxidation products through the activated carbon when abatement progresses. A water-washing procedure for regeneration of carbon catalyst is suggested. The evaluation of the type of activated carbon, and the initial concentrations of water in the catalyst and phosphine in air, the gas flow rate through the catalyst and the relaxation of the catalyst is presented. The compositions of phosphine oxidation/trapping catalysts and procedures for their syntheses were developed. The activities of these catalysts exceeded that of the Centaur carbon. These catalysts can be regenerated by removing the products and re-doping the catalyst with ammonium and/or potassium iodide.

Results and discussion

Environmental preservation concerns require removal of phosphine from air contaminated during fumigation of grain or tobacco warehouses. The procedure, currently applied in industry, usually includes the filtration of air pumped from a warehouse at a flow rate up to ~ 2000 hrs^{-1} through the activated carbon - based catalyst. This treatment of air involves phosphine oxidation, primarily to phosphoric acid. The oxidation products usually remain entrapped in the catalyst.

The number of the published studies of a very complicated process of an oxidative entrapment of phosphine is quite limited. The most recently published studies [1-19] are referenced here. Although the above mentioned entrapment by activated carbon appears to be a very efficient abatement method, several complications exist, for example a possible self-overheating of a catalyst at high inlet PH_3 concentrations or unpredictable variations in the catalyst capacity. The presented study was undertaken to understand more about the principles involved in this process and to develop a phosphine removal system, free of these drawbacks.

Several catalyst systems were developed and studied in the course of this work: fresh, aged and water-washed activated carbons, NH_4I, NH_4OH, KI, NaCl, $CuCl_2$ and KBr doped carbons. Two types of commercially available activated carbon, i.e. a chemically activated carbon and a steam activated carbon, are considered for the preparation of these catalysts.

The laboratory scale catalysis studies were performed in a gas-flow tube reactor of glass having 250 ml-volume, equipped with a fused glass filter-shelf to hold typically 100 ml catalyst sample, and a thermocouple pocket extending through the catalyst bed. The thermocouple provided measurements of the exothermicity of the oxidation reaction profile along the phosphine-containing gas passing through the catalyst. This measurement provided an indication of the completion of the saturation of a

catalyst layer by phosphoric acid, as the active zone of catalyst moved with the gas flow. The typical time dependence of PH_3 conversion is shown in Figure 1. These results illustrate the catalysis on the most active supported ammonium iodide catalyst compare to the untreated activated carbon from Norit.

The concentration of phosphine was measured by a Varian Chrompack CP2003 Micro GC, which was continuously monitored and the data recorded via a remote computer. Gas was drawn through the phosphine-containing gas chamber and pushed to the flow meter, reactor and GC gas-sampling loop by a gas pump. Reaction gas from the reactor was then returned to the phosphine chamber.

The phosphine/air mixture was prepared in a 33 m^3 stainless steel chamber using the hydrolysis of aluminum phosphide by atmospheric water. The resulting typical maximum concentration of phosphine varied from 50 to 2000 ppm. The progressing slow gas-phase oxidation of phosphine was considered for the kinetic measurements and for the estimations of various homo- and heterogeneous decay processes in the warehouses, as well as the leakage rate.
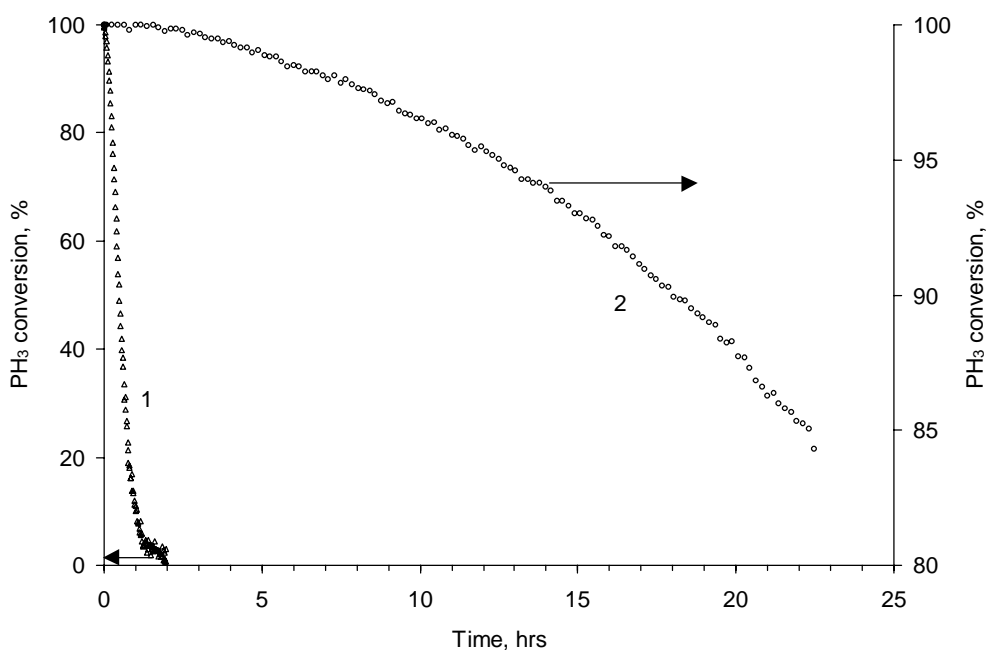

Figure 1   Removal of phosphine from 2 L/min air with 550 ppm PH_3 by 50 ml SAC Norit RB4 activated carbon without (curve 1) and with NH_4I (2).

Industrial scale experiments were performed also in the field with a two-bed vertical canister-type steel reactor 176x216 cm, loaded with 1200 kg Centaur HSV 4x6 mm catalyst, equipped with the pulling fan with capacity of 57 m^3/min, mounted atop of the canister. Air containing 200-300 ppm phosphine was taken from a just fumigated tobacco warehouse of approximately 28,000 m^3 volume. The straight warehouse-reactor-atmosphere system and the recirculation warehouse-reactor-warehouse system were applied and studied.

Temperatures, phosphine concentrations, pressures and air flows were monitored in the key points of the abatement system. The typical dependence of the outlet concentration of phosphine during the initial period of catalytic abatement is shown in Figure 2 for fresh, once-used and twice-used HSV catalyst. The unsteady process is explained in terms of accumulation of necessary intermediate compounds.

This study revealed that the phosphine catalytic oxidation/adsorption process is a complex system involving a fast adsorption of phosphine, chemical reactions of surface compounds and slow diffusion of both phosphine and oxidation products through the

activated carbon. The oxidation products always remain within a catalyst zone. The development of a kinetic model of such a process requires evaluation of the most significant variables, i.e., the type of activated carbon, the initial concentrations of water in the catalyst and phosphine in air, the gas flow rate through the catalyst and the relaxation of the catalyst. The evaluation of these variables is presented in this work.
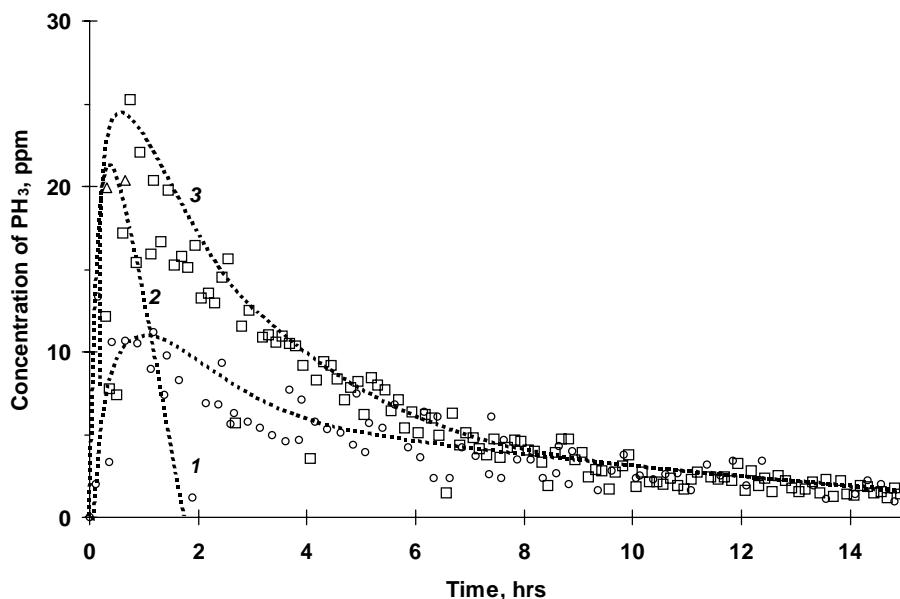

Figure 2   Adjusting to a steady-state concentration of phosphine in the outlet gas of the industrial reactor during the initial period of its work. Fresh Centaur HSV 4x6 mm catalyst (1), the same catalyst after defumigation of first 28,000 m^3 - warehouse (2), after second warehouse (3). All experiments are at the phosphine inlet initial concentration of 200 ppm.

Water was found to be an important participant of the overall process, possibly by hydrolyzing the intermediates and/or controlling their adsorptivity and diffusion through the catalyst. The initial concentration of water in the catalyst may affect both a long-term catalyst activity, and the presence of the initial induction period of self-activation of a catalyst in the reaction gas. Gas flow rate determines the rate of accumulation of products, always leading to a transfer from the fast chemical kinetics-controlled process to a slow diffusion through the catalyst-controlled process.

This situation is complicated by an additional difficulty for condensed phosphoric acid to diffuse. Dependence of the phosphine conversion of time at the different air flow rates, shown in Figure 3, supports this conclusion. Initial concentration of phosphine in air also determines the rate of phosphoric acid formation, therefore, complicating the macrokinetics of the process. Relaxation of the

catalyst between consecutive runs may improve its performance because the products will be provided a time to diffuse deeper to free more active sites on the surface.

The total catalyst capacity depends on the concentration of phosphine in the inlet gas. This capacity dramatically decreases when PH_3 concentration exceeds approximately 800 ppm at a flow rate of the order of 1000 hrs^{-1}. The phenomenon is explained by the limitation of H_3PO_4 diffusion through the solid catalyst and the limitation of PH_3 diffusion through the formed liquid acid; both these limitations arise from the rapid formation of liquid hydrated phosphoric acid, which blocks the surface of the carbon-based catalyst.

The formation of the phosphoric acid reaction product also causes an increase in water affinity of the catalysts. As a result, the amount of water from passing air trapped by the catalyst may reach 60 % of

its weight; this weight corresponds to the molecule $H_3PO_4*4H_2O$, deposited in the catalyst.

The possibility of the periodic re-activation of a partially deactivated catalyst by the deposition of a small amount of iodine vapor was observed. However, an excessive amount of atmospheric water was found to be a major complication to the long-term use of the carbon-based catalyst. This water accumulated in the catalysts in molar amounts thirty times the trapped phosphine, so that nearly the total pore volume of the catalyst became filled with water.

Re-circulation of the phosphine-containing gas back to the warehouse and/or the installation of a heater in the incoming reactor gas stream is suggested to keep the catalyst relatively dry and active in the oxidation of phosphine and in retaining the phosphoric acid reaction product. This was found to dramatically prolong the catalyst lifetime.

The catalyst regeneration procedure, composed of water-washing followed by drying in airflow at 40-70°C, was developed and studied. The above-suggested recirculation of the phosphine-containing gas back to the warehouse was successfully applied and combined with this regeneration.
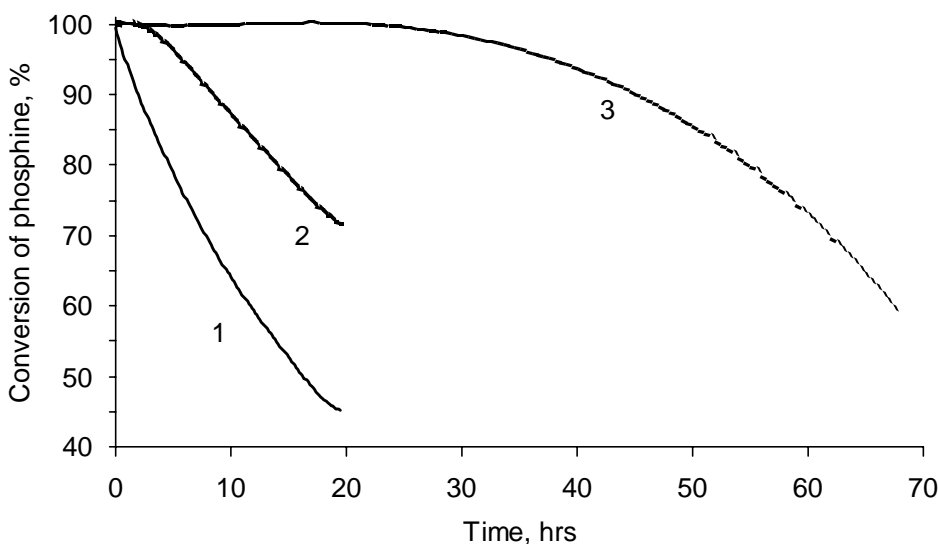

Figure 3 Removal of phosphine from 5.6 L/min (curve 1), 2.8 L/min (2) and 1.4 L/min (3) air with 370 ppm PH_3 by 50 ml NH_4I on EI46P activated carbon.

Transfer of the abatement system from a process, controlled by the gas flow rate provided by the reactor's fan, to a process, controlled by internal diffusion of PH_3 through the materials stored in a warehouse was found. This suggests the optimal capacity of the fan for the PH_3 abatement industrial reactor, which can be efficiently applied to a particular warehouse loaded with, for example, grain bags or wrapped bales of tobacco.

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