Flow-through catalytic membrane reactors for the destruction of a chemical warfare simulant: Dynamic performance aspects

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A B S T R A C T

A model was developed to describe the dynamic performance of a flow-through catalytic membrane reactor (FTCMR) used for the destruction of a chemical warfare agent (CWA) simulant, specifically dimethyl methylphosphonate (DMMP). For such a reactor, after a certain time period during which it provides full protection, its performance begins to decline, as manifested by a gradual decline in the thermocatalytic destruction rate of the DMMP and discernible changes in the membrane's throughput. The model ascribes these phenomena to changes in the catalytically active membrane surface area and in the accessible membrane pore volume, which are brought upon by the deposition of phosphorous-containing by-products of the DMMP's thermocatalytic decomposition reaction. Such a hypothesis is supported by experimental data for both fresh and aged membranes that substantiate significant losses in surface area and pore volume, and indicate the presence of phosphorous in the aged membranes. The model was used to fit the experimental data from a FTCMR operating under a total flow-through (100% stage-cut) mode of operation, and was shown to describe well the experimental data. In addition, the model was utilized in a predictive mode to describe the performance of a FTCMR employing another membrane from the same batch and catalytically activated under the same procedure, but operating under different operating conditions (0% stage-cut). The model was shown to provide an adequate fit to the experimental data. Following such validation, the model has been used to gain further insight into the impact of the various reactor parameters on FTCMR performance. Its use has, subsequently, led to the development of a novel reactor configuration that significantly expands the operating performance window of the FTCMR for the thermocatalytic CWA destruction.

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1. Introduction

Flow-through catalytic membrane reactors (FTCMR) have shown promise for different applications due to their ability to minimize intraparticle mass transfer resistance, and to provide higher catalytic reaction rates and better catalyst utilization [1]. However, due to their unique mode of operation, involving dead-end flow, any obstruction to flow caused by the reaction may directly affect their performance, since under a fixed operating reactor pressure this causes the membrane permeation flux to decline. Such obstruction can be caused, for example, by the physical deposition of solid reaction by-products inside the pores, or from side reactions with the pore walls themselves to produce a stable solid material blocking the membrane's pore structure.

A key focus of the authors in recent years has been the use of FTCMR for the removal of chemical warfare agents (CWA) from contaminated air streams. Experiments have been carried out with dimethyl methylphosphonate (DMMP), a simulant for Sarin (GB), which is a powerful CWA [1]. Multi-tubular FTCMR have been constructed and tested [2], and shown to provide complete protection against DMMP (conversions >99.99%) with acceptable (<1 kPa) pressure drops with (protection) times almost an order of magnitude longer than those offered by the "state-of-the art" conventional adsorption systems. Beyond a certain time of FTCMR operation, however, the continuing increase in the resistance to flow through the membrane, caused by the thermocatalytic reaction interferes with reactor operation [3]. During laboratory testing for a dead-end (100% stage-cut) mode of operation under constant feed-flow conditions, what one observes is a gradual increase in feed pressure mirroring the decrease in membrane permeance. For example, Fig. 1 shows the data with a FTCMR operating at 623 K with a DMMP feed concentration of 300 ppm$_v$. The asymmetric

inorganic membrane used for this test had an effective length of 70 mm, and consisted of an α-Al_2O_3 support tube with an average pore size of 0.4 μm, an intermediate α-Al_2O_3 layer with an average pore size of 0.05 μm, and a top γ-Al_2O_3 film with a average pore size of 0.01 μm. The thickness of the support, intermediate, and separation layers were ca.1100, 15, and 2 μm respectively, as measured by a scanning electron microscope (SEM).

The rate by which pore blockage occurs and its impact on the FTCMR performance has been shown experimentally to depend on system and operating variables such as the membrane's transport and catalytic characteristics, the mode of reactor operation (e.g., dead-end flow vs. operating at less than 100% stage-cut), the challenge (i.e., feed) CWA concentration, the feed flow rate, pressure, etc. For example, the CWA concentration exerts a strong influence on performance, with higher concentrations resulting in faster declines in membrane permeation rates [3]. A means to potentially extend the window of operation of the FTCMR, then, is to add a bulk CWA removal step as stage I preceding the FTCMR that substantially lowers the CWA concentration into the FTCMR, thus significantly extending its operating range. This team, in fact, has utilized such a hybrid device that combines a surface flow membrane (SFM) based system [3] together with a FTCMR that shows exceptionally long protection times towards the aforementioned model CWA.

The potential downside of such system is its added technical complexity, which may not be such of a problem for collective protection (CP) systems, but could be a challenge for small-scale individual protection (IP) devices. There is strong incentive, therefore, to continue to optimize the performance of stand-alone (but also the hybrid) FTCMR systems, so that protection times are maximized and requisite pressure drops are minimized. To accomplish that a better understanding of the factors and causes of the reduction in permeance and reactivity of the FTCMR must be gained, and a model must be developed accounting for such phenomena and their influence on performance. The development of such a model and its experimental validation is a key focus of the present investigation.

A better understanding of the phenomena responsible for changes in structure and reactivity during the decomposition of CWA is equally important for the more conventional reactors, since similar phenomena have been reported during the operation of these systems as well. Tzou and Weller [4], for example, studied the catalytic oxidation of DMMP in air over Pt/Al_2O_3 catalysts in a fixed-bed reactor. They reported a decrease in the catalyst's activity with time on stream; in addition, characterization of the deactivated

catalyst provided evidence that the alumina support had reacted with a reaction by-product (reportedly H_3PO_4) to generate $AlPO_4$. Cao et al. [5,6] investigated the thermocatalytic decomposition of DMMP on activated carbon (AC), and also on Ni, Fe, Cu, and V catalysts supported on various metal oxides including MgO, Al_2O_3, SiO_2, and TiO_2. For the AC, BET analysis of both the fresh and the spent catalysts indicated sharp decreases in pore volume and surface area during the course of the reaction, due to large amounts of coke and phosphorus-containing species occupying the pores. Analysis of the latter species via ion chromatography (IC) suggested that they are, most likely, P_2O_5 or H_3PO_4. Substantial losses in BET surface area were also observed with all the supported catalysts. The coke was attributed to the dehydration of DMMP and methanol (a by-product of the DMMP decomposition reaction) on the deposited P_2O_5.

In fact, the pore-blockage and deactivation phenomena observed with DMMP, have been previously reported during the thermocatalytic oxidation of numerous other P-containing compounds over the past four decades. In one of the earliest studies, McArthur [7] investigated the degradation of engine exhaust de-NO_x catalysts due to phosphorous-containing compounds originating in the engine oil and fuel. He suggested a mechanism for catalyst degradation that involves adsorption of P_4O_{10} and/or P_4O_6 on the catalyst surface, followed by reaction with co-adsorbed H_2O to form H_3PO_4, and then by reaction between H_3PO_4 and the catalyst to form hydrothermally-stable phosphate compounds. Hegedus and coworkers [8,9] studied the interaction of phosphorous-containing compounds in engine exhaust with Pt/Al_2O_3 catalysts via electron microprobe analysis. The poisons were shown to penetrate the catalyst pellets as progressing sharp shells with phosphorus accumulation controlled by pore diffusion. The phosphorus appeared to form as a monolayer over the pore surfaces, with little impact on the effective diffusivity. It was reported that H_3PO_4 acted as a precursor for the surface phosphorous, and upon entering the pores of the catalyst it had preferred to diffuse past the already poisoned shell to react with the fresh catalyst. Eaton [10] investigated the phosphorus poisoning of Pt/Al_2O_3–CeO_2 diesel oxidation catalysts (DOC) by the lube-oil additive zinc dialkyl-dithiophosphate. Phosphorus was found confined to the uppermost layer of the washcoat. He reported the presence of $AlPO_4$ within the DOC washcoat, and theorized that its formation was the initial step leading to the incorporation of phosphorus into the washcoat. Kröger et al. [11] also studied the effect of phosphorous poisoning on the catalytic activity of Pt-type DOC prepared with various oxide supports including ZrO_2, Al_2O_3, CeO_2,
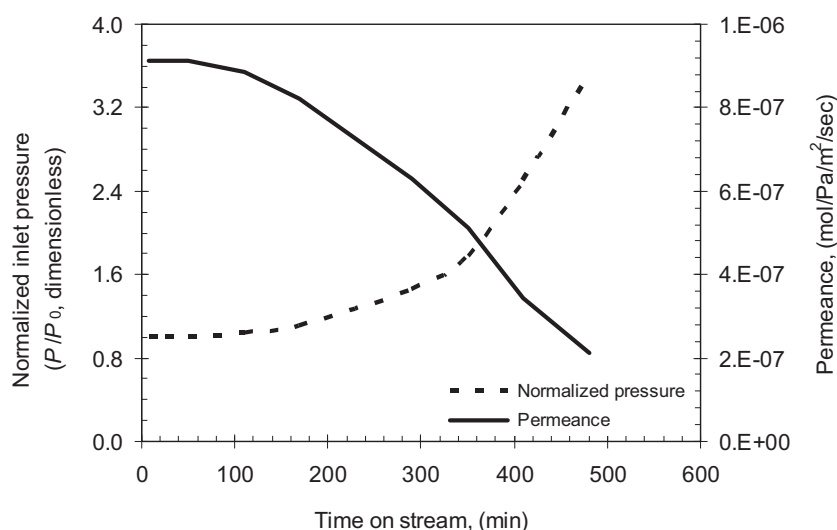

Fig. 1. Permeance decrease during the DMMP destruction at 673 K (DMMP load: 300 ppm$_v$).