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Thermocatalytic Decomposition of Dimethyl Methylphosphonate on Activated Carbon

Lixin Cao,* Steven L. Suib,*,[1] Xia Tang,† and Sunita Satyapal†

**U-60, Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-3060; and †United Technologies Research Center, 411 Silver Lane, East Hartford, Connecticut 06108*

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Activated carbon was used for the catalytic decomposition of dimethyl methylphosphonate (DMMP), a simulant of nerve gases, at various temperatures. Under the same conditions, activated carbon exhibited better longevity than a platinum catalyst, which has been widely chosen for this reaction. Nitrogen adsorption measurements at 77 K indicated that the majority of pores in the activated carbon were micropores, which could be transformed to macropores at 723 K in air. During the course of the reaction, large amounts of phosphorus species and coke occupied the pores, resulting in a sharp decrease in pore volume and surface area. Experimental results showed that the decomposition of DMMP involved two stages. In the first stage, activated carbon behaved as an initiator, converting DMMP into CO_2, methanol, and P_2O_5. This reaction required oxygen supplied from air. In the second stage, P_2O_5 that had accumulated in the reactor was able to catalyze the decomposition of DMMP. The second stage was actually an autocatalytic process. A two-stage reaction model of DMMP decomposition on activated carbon and other catalysts is proposed. © 2001 Academic Press

Key Words: **DMMP decomposition; activated carbon.**

INTRODUCTION

Dimethyl methylphosphonate (DMMP) has been used as a simulant of chemical warfare agents (CWAs) because of its similarity in physical and chemical properties to CWAs and feasibility in the laboratory (1). Currently, catalytic decomposition is still one of the most attractive methods for the disposal of CWAs as well as other organophosphorus pollutants. Platinum catalysts have been favorably employed for the thermocatalytic decomposition of DMMP (2–4), probably because of their excellent capability for completely oxidizing organic compounds. However, deactivation was observed on platinum catalysts, as well as on other catalysts reported in the literature (5). For practical purposes, a catalyst with long duration time, high reactivity, and cost efficiency is needed for the detoxification of CWAs.

In this paper, activated carbon was used for the decomposition of DMMP in the presence of air. In the literature (6), activated carbons with a typical nitrogen BET surface area of 400–1500 m^2/g and adsorption capacity of 0.6–0.8 cm^3/g are used extensively as adsorbents to purify, decolorize, deodorize, and decontaminate water and air. Activated carbons have also been used as effective adsorbents in the disposal of CWAs. The catalytic function of activated carbons for the oxidation of pollutants has not yet been investigated since oxygen is able to burn away the major carbon skeleton of activated carbons at high temperature. Our studies showed that the apparent longevity of an activated carbon catalyst for DMMP decomposition was much better than that of a Pt/Al_2O_3 catalyst. Smentkowski *et al.* (7) previously discussed the heterogeneous catalytic oxidation of organophosphonate esters using a molybdenum catalyst. It is stated that the reaction results in the production of CO and phosphorus oxide(s) without the undesired accumulation of carbonaceous or phosphorus overlayers on the Mo surface. In fact, Mo is one of the few species shown to be resistant to poisoning by phosphorus compounds. However, the work states that the process must be carried out at a minimum of 900 K (627°C) and in the presence of excess oxygen. The catalysts described herein and in an additional publication (8) require operating temperatures roughly 200 K lower than those of the Mo catalysts, and yet show virtually no deactivation, thereby improving the feasibility of catalytic organophosphonate destruction.

EXPERIMENTAL SECTION

Catalysts

The activated carbon used in this study was obtained from Strem Chemicals, Inc. The granular activated carbon was cracked into 28–48 mesh particles for activity tests. The BET surface area for this sample was 897.5 m^2/g, and its pore volume was 0.6033 cm^3/g. After being degassed at 300°C for 10 h, the activated carbon lost 18.5% of its weight due to water desorption.

A 1% Pt/Al_2O_3 catalyst was prepared as follows and used as a reference for comparison of catalytic activity with that of activated carbon. $Pt(acac)_2$ was dissolved in ethanol. A γ-Al_2O_3 support obtained from Davidson was added to the

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[1] To whom correspondence should be addressed.

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solution. After being stirred at room temperature for 6 h, the solution was evaporated and dried at 120°C. The sample was calcined at 450°C for 6 h, and then pelletized and sieved into 28–48 mesh granules for activity tests. The nitrogen BET surface area of the catalyst was 284.3 m^2/g.

Apparatus

Evaluation of the catalyst was carried out in a fixed-bed reactor with an inner diameter of 4 mm. Ultra-high-purity air was used as a carrier gas which was flowed through a bubbler filled with DMMP at a flow rate of 50 ml/min in order to create a saturated DMMP vapor stream. The concentration of DMMP in the stream at 298 K was 1300 ppm (1 Torr). A mass of 0.100 g of the activated carbon was used for each test. The desired temperatures were obtained in a tubular furnace and controlled with a temperature controller. Two GCs were used for on-line analysis. One GC equipped with an FID and RTX-5 column (RESTEK Corp.) was used for analyzing dimethyl ether, methanol, DMMP, and other organic compounds. The other GC equipped with a TCD and Carboxen column (Supelco) was used for detecting CO and CO_2.

Characterization Methods

Measurements of the nitrogen BET surface areas and adsorption isotherms were conducted using an ASAP 2010 instrument supplied by Micromeritics. After being degassed for 2 h at 100°C and for 10 h at 300°C under vacuum, samples were cooled to ambient temperature and transferred to the adsorption port.

XPS data were obtained with a Physical Electronics ESCA System, Model 5400, equipped with a Mg anode, a hemispherical analyzer, a position-sensitive detector, and an Omni-focus lens (nominal area diameters $= 1.1$ mm and 0.6 mm). All spectra were corrected for sample charging by referring the C1*s* photoelectron line for adventitious carbon to 284.8 eV.

Aqueous extraction for ion chromatography analysis was accomplished by extracting the used catalyst in warm H_2O for at least 2 h. The solutions were then treated with ultrasound for 10 min and filtered through a 0.22-μm filter. The ion chromatography system contained a Dionex DX 500 ion chromatography pump, a Dionex AS4A-SC anion exchange column, and a CD 20 conductivity detector. The eluent contained 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$, at an approximate pH of 10.

RESULTS

Reactivity of Activated Carbon

Before the activity tests were made, the following blank or background tests were conducted. A reactant mixture of DMMP (1300 ppm) and air with a flow rate of 50 ml/min was passed through an empty reactor at 723 K. No gas phase decomposition of DMMP was observed. An activated carbon catalyst was then loaded into the reactor and DMMP vapor was passed through the reactor under the same conditions using helium as a carrier gas, instead of air. The outlet DMMP concentration returned to its inlet level at 723 K after 1 h, showing that the adsorption equilibrium of DMMP on the activated carbon was reached within 1 h and no decomposition of DMMP took place in the absence of oxygen.

The decomposition of DMMP in the presence of air was run under the following reaction conditions: a flow rate of 50 ml/min with a mixture of air and DMMP (1300 ppm) and temperatures ranging from 573–723 K. The terms "protection time" or "protection period," representing the duration of 100% conversion of DMMP, are used to evaluate the performance of each catalyst (5). Note that detection limits were approximately 0.1% and therefore the conversion verified is nominally 99.9%. After passing the protection period, the catalyst begins to deactivate. The platinum catalyst had been studied in different laboratories (2–5) and exhibited good catalytic activity and was chosen as a reference to compare to the activated carbon in this study.

The conversion of DMMP versus time course on the 1% Pt/Al_2O_3 catalyst and activated carbon is illustrated in Fig. 1. The protection time of the activated carbon was strongly dependent on the reaction temperature. At 573 K, the activated carbon lost its activity very quickly. However, protection times obtained at high temperatures were 10 h for 623 K, 26 h for 673 K, and more than 100 h for 723 K. At 673 K, after the catalyst passed through the protection period, the conversion of DMMP fell to 99.0%, and then increased and fluctuated between 99.5% and 100% even though the catalyst was run for 100 h. The same trend

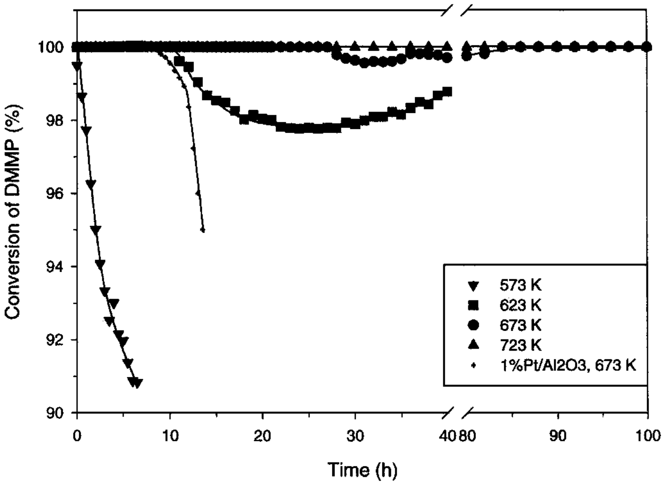

FIG. 1. Time course of DMMP conversion over the activated carbon and platinum catalysts at different temperatures. Inlet DMMP concentration, 1300 ppm; total flow rate, 50 ml/min.

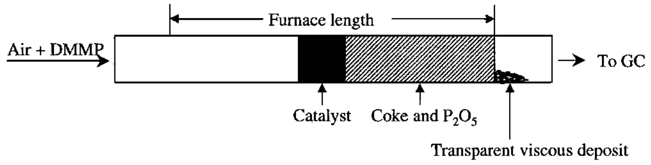

FIG. 2. Reactor after 100 h of operation.

occurred for the catalyst operated at 623 K. The cause of this abnormal behavior which is due to the complexity of the process will be further described in the Discussion section. The protection time of the activated carbon in this study should be termed an "apparent" protection time, because it involved not only the protection time of the activated carbon but also that of the P_2O_5 product formed in the reaction. Compared with the protection time of the activated carbon at 673 K, the platinum catalyst exhibited much shorter longevity (8.5 h).

After the activated carbon was used at 673 and 723 K for 100 h, coke and a viscous material were observed inside the reactor (Fig. 2). In the catalyst bed, the original activated carbon catalyst in the form of 28–48 mesh granules became a solid body, which was difficult to remove from the reactor. From the end of the catalyst bed to the border of the furnace, coke and the viscous material were deposited onto the reactor wall. Outside the furnace, the transparent viscous material was condensed on the reactor wall. The coke and viscous material were washed with water and the solution was analyzed using ion chromatography. Analytical results showed that the sample contained a large amount of PO_4^{3-}, suggesting that the viscous material was P_2O_5 or phosphoric acid.

Figure 3 shows the methanol distribution in the reaction products versus time. On the platinum catalyst, no effluent methanol was detected during the protection period. The methanol concentration increased drastically after the catalyst began to lose its activity. However, the behavior of the methanol concentration on the activated carbon was totally different. In the initial stage of the reaction, methanol concentrations decreased at 573–673 K. They then increased at temperatures of 623 K and 673 K. Since activated carbon deactivated very quickly at 573 K, it was only run for 7 h. The volcano-shaped curve for the methanol distribution might have been observed as well if the reaction were run for a longer time at 573 K. At 723 K, only a small amount of methanol was detected. The methanol distribution curves in Fig. 3 indicated that more methanol was released at lower temperature. The decrease in methanol concentrations with temperature was caused by an increase in the catalytic effect of P_2O_5, one of the products from the DMMP decomposition.

CO_2 distribution is another important parameter for the oxidation of DMMP. In this study, CO_2 was formed from two sources: the reactant (DMMP) and the catalyst (activated carbon). In order to obtain the net CO_2 produced from DMMP, blank experiments were designed. Air with a flow rate of 50 ml/min in the absence of DMMP vapor was passed through activated carbon at 573, 623, 673, and 723 K. The effluent CO_2 concentrations are shown in Fig. 4. At low temperatures (573 and 623 K), very little CO_2 was released from the activated carbon. However, if the temperature was as high as 723 K, a large amount of CO_2 was observed at the beginning of the reaction. The "burnout" of surface carbon species exposed to oxygen was responsible for the generation of CO_2 in this case; definitely, high temperature boosted the burnout rate. No CO was detected at temperatures ranging from 573 K to 723 K. These results demonstrated that the activated carbon was not stable at 723 K in a flowing air stream and a weight loss as high as 60% was observed after 14 h. By subtracting the CO_2 amounts

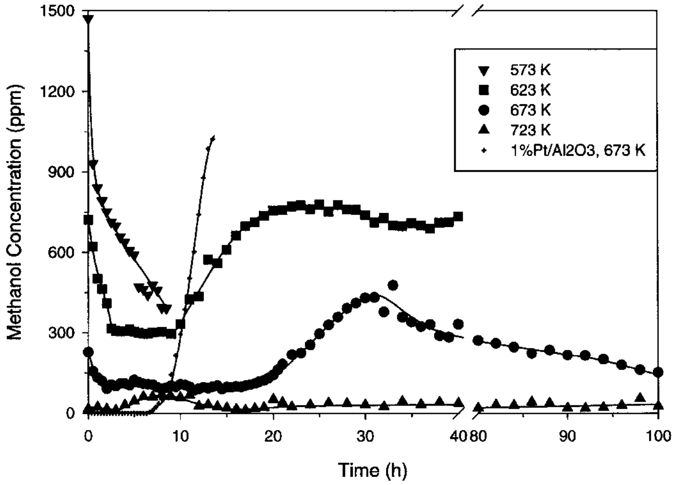

FIG. 3. Methanol concentration as a function of time on stream. Inlet DMMP concentration, 1300 ppm; total flow rate, 50 ml/min.

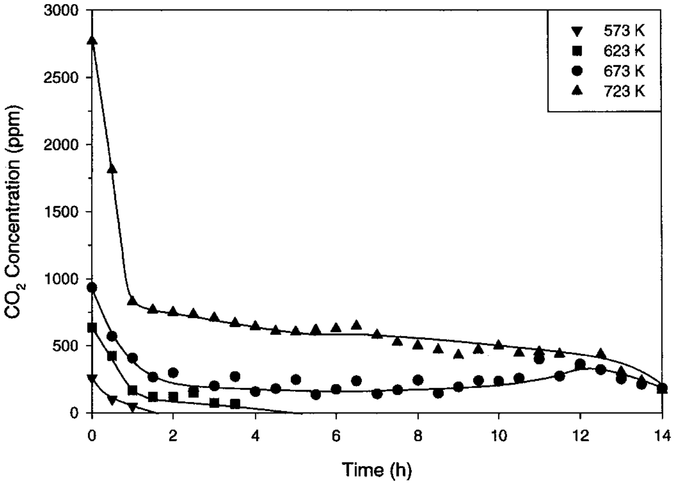

FIG. 4. CO_2 concentration as a function of time on stream in the absence of DMMP. Air flow rate, 50 ml/min.

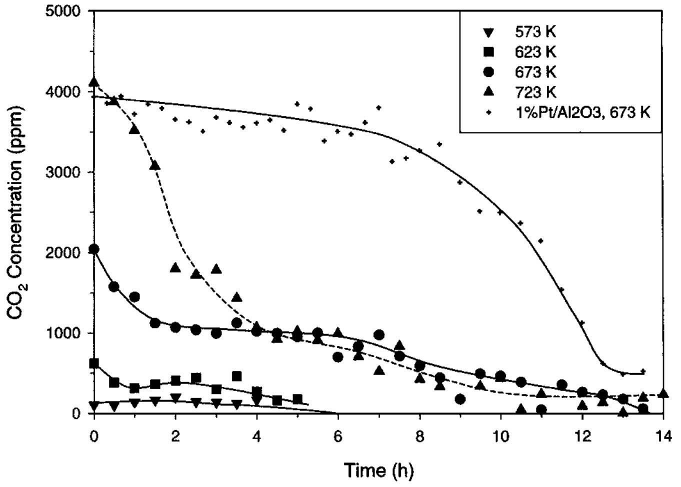

FIG. 5. Net CO_2 concentration as a function of time on stream for the decomposition of DMMP. Inlet DMMP concentration, 1300 ppm; total flow rate, 50 ml/min.

released from activated carbon from the total CO_2 amounts, the net CO_2 concentrations generated from DMMP were obtained and are presented in Fig. 5. On the platinum catalyst, the carbon balance, the combination of methanol and CO_2 concentrations, reached approximately 100% during the protection period. The concentration of CO_2 decreased with loss of catalytic activity. This is a general trend for the oxidation of DMMP (5). However, the carbon balance of the activated carbon at different temperatures calculated in this study was far from 100% except in the initial stages at 723 K. An accumulation of coke deposit was observed in the catalyst bed, as well as on the reactor wall, showing that a large part of the carbon in DMMP was converted to coke in this case. The coke is believed to be formed via dehydration of DMMP and methanol on P_2O_5 since P_2O_5 is a strong desiccant, capable of extracting water from oxygen-bearing organic compounds.

Measurements of BET Surface Area and Adsorption Isotherm

Activated carbons are porous materials with high surface areas and porosities. Their textural properties are very important when they are used as adsorbents or catalysts. The N_2 adsorption isotherm of the samples are shown in Fig. 6. Sample B is the untreated activated carbon, which was used as a reference for the rest of the samples. The activated carbon treated with flowing air at 673 K for 14 h (sample A) has the highest adsorption capacity. However, the adsorption capacity decreased sharply after the activated carbon was treated at 723 K (sample E). This could be due to the collapse of the micropores in the samples caused by the combustion of the carbon species. Samples C and D are activated carbon catalysts that were previously used for DMMP oxidation for 1 and 3 h. Their adsorption capacity decreased with increasing reaction time. The shape of the isotherm and the appearance of the hysteresis loop demonstrate that the activated carbon used in this study is abundant in micropores and mesopores.

The BET surface areas and pore size distributions of the samples are listed in Table 1. Pores are classified as micropores for $d < 2$ nm, mesopores for $2 \leq d \leq 50$ nm, and macropores for $d > 50$ nm (9). The Horvath–Kawazoe method (10–12) was employed in the measurement of micropores since it had been widely and rapidly adopted in recent years. The classic BJH desorption method (13) was employed in the measurement of mesopores and macropores. The majority of pores in the untreated activated carbon are micropores. After the activated carbon was treated in flowing air at 673 K for 14 h, the number of micropores mesopores, and macropores increased. Correspondingly, the BET surface areas increased from 897.5 to 1018.9 m^2/g. A burnout of carbon species may create new micropores. At the same time, more mesopores and macropores are developed by the burnout of the walls between the adjacent pores. The continuous evolution of CO_2 from the activated carbon at 673 K shown in Fig. 4 gives evidence of this burnout process. After treatment at a higher temperature (723 K), the activated carbon lost the majority of its micropores as its surface area and total pore volume decreased from 897.5 to 241.3 m^2/g and 0.4283 to 0.1033 cm^3/g, respectively. There is no significant difference in mesopore volume, but the macropore volume increased slightly from 0.0079 to 0.02 cm^3/g. This shows that high temperatures accelerate the burnout of carbon species in the sample, which is again consistent with the result of an increase in CO_2 released from the activated carbon as shown in Fig. 4.

After treatment with DMMP at 673 K in the presence of oxygen, activated carbon lost its surface area and porosity

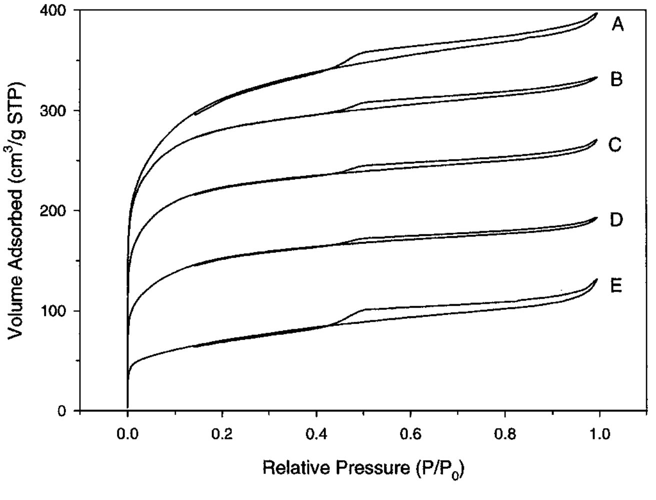

FIG. 6. Isotherms of activated carbon treated under different conditions: (A) treated with flowing air at 673 K for 14 h; (B) untreated; (C) treated with DMMP at 673 K for 1 h; (D) treated with DMMP at 673 K for 3 h; and (E) treated with flowing air at 723 K for 14 h.

TABLE 1

Textural Properties of Activated Carbon Treated under Different Conditions

Sample	Micropore volume (cm^3/g) (<2 nm) (Horvath–Kawazoe)	Mesopore volume (cm^3/g) (2–50 nm) BJH desorption	Macropore volume (cm^3/g) (>50 nm) BJH desorption	Total pore volume (cm^3/g)	BET surface areas (m^2/g)
AC-untreated	0.4283	0.1670	0.0079	0.6033	897.5
AC-673 K in air for 14 h	0.4696	0.2874	0.0144	0.7714	1018.9
AC-673 K in DMMP for 1 h	0.3400	0.1401	0.0124	0.4925	713.8
AC-673 K in DMMP for 3 h	0.2301	0.1300	0.0096	0.3697	497.8
AC-673 K in DMMP for 5 h	—	—	—	—	1.2
AC-723 K in air for 6 h	0.1033	0.1560	0.0200	0.2793	241.3

rapidly, especially microporosity (samples C and D). Under these conditions, P_2O_5 produced by the complete oxidation of DMMP must have blocked or occupied the micropores first. Although the sublimation point of P_2O_5 is only 623 K, the slow diffusion of P_2O_5 causes the pores to become filled or blocked with phosphorus species. The catalyst completely lost its surface area within 5 h, but its catalytic activity persisted at a high level for 26 h. The continuing activity after the loss of surface area of the activated carbon can be attributed to the catalytic activity of P_2O_5, which is the reaction product of DMMP on the activated carbon catalyst.

X-Ray Photoelectron Spectroscopy

XPS was used to identify the species on the used activated carbon and the spectra are shown in Fig. 7. From a comparison of these two spectra, it can be seen that the surface of the activated carbon reacted at 723 K contains less carbon and more oxygen and phosphorus species. This is consistent with the results of the CO_2 evolution and isotherm measurements shown in Figs. 4 and 6. The binding energies of phosphorus on the spectrum correspond to PO_4^{3-} (14), as the hydrolysis product of P_2O_5 formed in the reaction is likely responsible for the marked increase in phosphorus and oxygen peak intensities on sample B.

Ion Chromatography

Ion chromatography (IC) was employed to investigate the content of phosphorus species on the activated carbon samples. All samples presented in Table 2 were pretreated with a flowing air stream mixed with saturated DMMP vapor for 5 h. According to the isotherm results, activated carbon treated under such conditions lost its surface area completely. The content of DMMP cannot be measured by IC because DMMP is nondissociatively dissolved in water and the prerequisite for success of this method is the formation of ions in aqueous solution. Table 2 indicates that the content of PO_4^{3-} originating from phosphoric acid or P_2O_5 increases with reaction temperature, while the content of methylphosphonate acid (MPA), in which the P–CH_3 moiety is intact, decreases. Previous studies (15–17) have confirmed that the cleavage of P–CH_3 requires high temperatures because of the high bonding energy. Our results are in good agreement with this conclusion. At low temperatures, DMMP was partially oxidized into

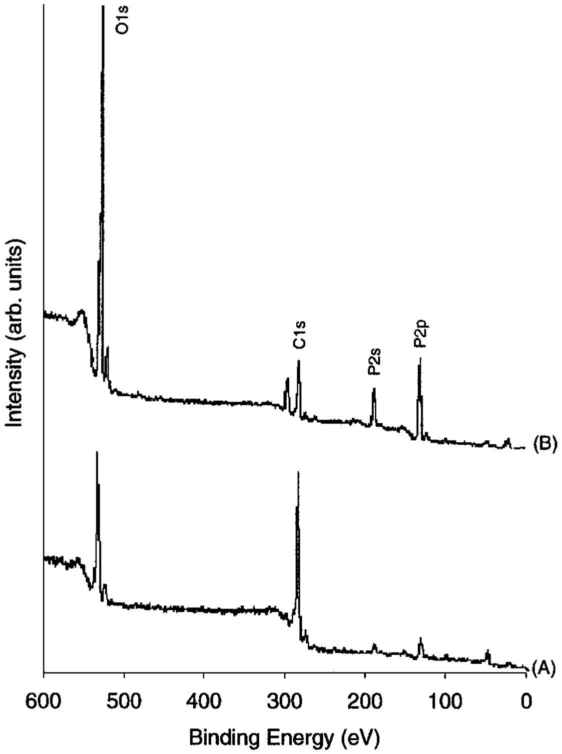

FIG. 7. XPS results for activated carbon samples used for DMMP decomposition for 5 h: (A) 673 K and (B) 723 K.

TABLE 2

Ion Chromatography Results

Sample-temperature	PO_4^{3-}	MPA	MMP
AC-573 K	13.59 (mg/g)	86.42 (mg/g)	Small amount
AC-623 K	52.01 (mg/g)	40.43 (mg/g)	N/D[a]
AC-673 K	99.14 (mg/g)	3.95 (mg/g)	N/D
AC-723 K	116.47 (mg/g)	0.93 (mg/g)	N/D
White fog	2.63 (ppm)	90.44 (ppm)	Small amount

[a] N/D, nondetected.

MPA through the breaking of two methoxy groups. With increasing the reaction temperature, the adsorbed MPA was converted to P_2O_5 via breaking of the P–CH_3 bond. Obviously, high temperature facilitates the oxidation of DMMP. A small amount of methyl methylphosphonate (MMP) resulting from the loss of one methoxy group in DMMP was detected on the activated carbon treated at 573 K. No such compound was observed at temperatures higher than 623 K. During the reaction a white fog was observed to exit from the reactor. It was trapped in water for IC analysis, which showed that the white fog contained a small amount of PO_4^{3-} and some MPA. The reason the content of MPA in the white fog is higher than the content of PO_4^{3-} is that the majority of phosphoric acid or P_2O_5 formed in the reaction is condensed within the reactor because of its high sublimation temperature.

DISCUSSION

Activated carbons have a high degree of porosity, extensive surface areas, and reactive surface structures. The nonpolar carbon surface can selectively adsorb organic compounds. Consequently, activated carbon has been widely used for adsorption of many organic chemicals in water and air. Bansal *et al.* (18) studied the behavior of surface oxygen in a variety of activated carbons. They found that the adsorbed oxygen on activated carbon evolved as CO_2, CO, and water vapor under heat treatment. The evolution of CO_2 occurred in the temperature range of 573 to 973 K, but CO began to emit at comparatively higher temperatures of 773 to 873 K. In our study, CO_2 was detected when the reaction was run at temperatures ranging from 573 to 723 K. On the other hand, DMMP is adsorbed on many metal oxides via the interaction between P=O groups and the surface active sites which are believed to be Brønsted or Lewis acid sites (15). Bansal *et al.* (6) pointed out that acidic sites were developed on activated carbon as a result of surface oxidation. The optimum temperature for the development of acidity on activated carbon was found to be around 673 K. Our experiment confirmed that the oxidation of DMMP could not proceed on the activated carbon in the absence of molecular oxygen and the gas phase reaction between oxygen and DMMP could not take place without a catalyst. Combining their results with ours, it is concluded that the formation of acidic sites by the interaction of oxygen with surface carbon at elevated temperature facilitates the adsorption of DMMP on these sites via phosphoryl oxygen. The reaction between the adsorbed DMMP and oxygen gives rise to CO_2, methanol, and P_2O_5 formation in the initial stages of our reaction.

As shown in Fig. 1, the “apparent” protection time of the activated carbon at 673 K is 26 h, but the conversion of DMMP regains a level of 99% after a slight deactivation. However, the isotherm and BET surface area measurements indicate that the catalyst loses its porosity and surface area almost completely in the first 5 h. Such a contradiction inspired us to investigate the reaction between DMMP and the viscous product mixture of coke and P_2O_5 more carefully.

At first, the used activated carbon catalyst was removed from the reactor. The viscous material left in the reactor still caused a DMMP conversion as high as 95% at 673 K. A new reactor loaded with fresh P_2O_5 as a catalyst was then used for the reaction, and about 90% conversion of DMMP was obtained at 673 K. Coke was formed along the reactor wall and P_2O_5 condensed downstream. When helium was used as the carrier gas to replace air for a short time, similar experimental results were obtained at 673 K. Finally, methanol vapor, instead of DMMP, was added into the flowing air stream, and the mixture was passed through the P_2O_5 bed. A significant amount of coke was produced. The coke was identified to be graphite-type carbon. Further experiments confirmed that graphite exhibited no activity for the oxidation of DMMP.

The above experimental results show that P_2O_5 is an excellent catalyst for the decomposition of DMMP. P_2O_5 takes the place of activated carbon in the second stage of the process. Methanol is an intermediate of the DMMP decomposition reaction on P_2O_5, and the dehydration of methanol is subsequently responsible for the coke formation. This is because P_2O_5 is a very strong desiccant, which readily extracts water from oxygenated organic compounds. Both the decomposition of DMMP to form P_2O_5 and the methanol dehydration on P_2O_5 are temperature dependent. As a consequence, the higher the reaction temperature, the lower the methanol concentration in the effluent, as shown in Fig. 3. Only a very small amount of methanol has been detected in the effluent at 723 K, while a somewhat steady amount of methanol has been observed below 723 K. Since P_2O_5 is another major product of DMMP decomposition and is continuously produced from the reaction, the reaction catalyzed by P_2O_5 can be referred to as an autocatalytic process.

Due to the nature of the two-stage process, the apparent protection time of DMMP decomposition catalysts consists of two segments. One segment is represented by the activated carbon catalyst and the other by P_2O_5. Figure 8 shows

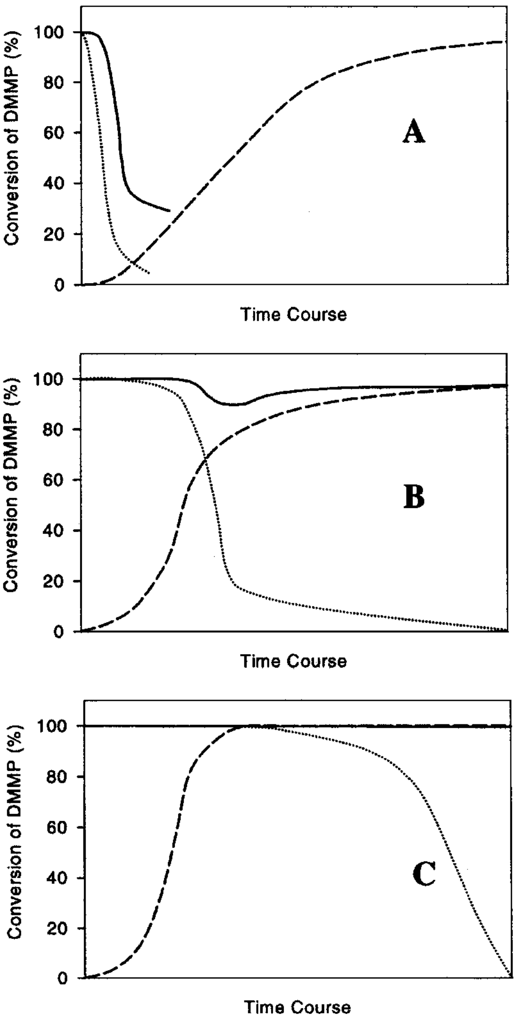

FIG. 8. Indicative diagrams for the catalytic processes of DMMP decomposition. Dotted line, original catalyst; dashed line, P_2O_5; solid line, overlap of the original catalyst and the subsequent P_2O_5 catalyst.

a general scheme of the apparent protection time of existing catalysts. For type A, the apparent protection time of the initial catalyst is short, and the P_2O_5 formed in the reaction is insufficient for the subsequent autocatalytic reaction. Catalysts, such as Pt/Al_2O_3 (2–4), Al_2O_3 (3), and MgO (19), belong to this type. During the reaction process, P_2O_5 is consumed by reacting with the metal oxides in the initial catalyst to form metal phosphates and becomes inactive for the reaction. Usually, the reaction is terminated soon after the abrupt loss of activity. For type B, the initial catalyst is more reactive and exhibits a longer protection time. Sufficient P_2O_5 is accumulated in the first stage. After passing its protection time the initial catalyst starts to deactivate abruptly. The deactivation of the initial catalyst is greater than the rise in activity originating from P_2O_5, so the DMMP conversion is lowered temporarily and then increases again. The performance of the activated carbon catalyst at 623 K and 673 K and the vanadium catalysts previously investigated in our laboratory (8) is similar to type B. For type C, the protection time of the initial catalyst is very long. The deactivation curve of the initial catalyst overlaps the rising curve of P_2O_5 activity, so the apparent protection is prolonged. The performance of the activated carbon catalyst at 723 K falls into this category.

Because of the complexity of DMMP decomposition, the above picture of the process on different catalysts is somewhat simplified. However, this two-stage reaction model for the thermocatalytic decomposition of DMMP not only explains the existing experimental results of various catalysts but also reveals important information for the exploration of new effective catalysts. An appropriate match of the catalytic properties of the initial catalyst and P_2O_5 seems essential for improving the performance of the catalyst. Detailed studies on the kinetics and mechanism of the DMMP decomposition on activated carbon and other catalysts are underway in our laboratory.

CONCLUSION

Activated carbon is a good catalyst for the decomposition of DMMP at temperatures above 673 K. The apparent protection time of the activated carbon is much longer than that of platinum catalysts. The activated carbon is relatively stable in flowing air at temperatures below 673 K. Activated carbon is burned and releases CO_2 at 723 K. After 5 h of reaction above 673 K, the activated carbon loses its porosity and surface area almost completely. However, the conversion of DMMP remains above 99% for 100 h. The prolonged apparent protection time is contributed to by both the activated carbon catalyst and the P_2O_5 formed in the reaction process. The activated carbon behaves primarily as an initiator for DMMP decomposition, producing CO_2, methanol, and P_2O_5. P_2O_5 accumulated in the initial stage then catalyzes the decomposition of DMMP, forming similar products. This autocatalytic reaction is temperature dependent since high temperature facilitates the cleavage of the $P–CH_3$ moiety. A two-stage reaction model has been proposed to explain the existing experimental results on various catalysts. Such a model may be helpful for the design and development of new effective catalysts for DMMP decomposition.

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