Thermocatalytic Oxidation of Dimethyl Methylphosphonate on Supported Metal Oxides

Lixin Cao,* Scott R. Segal,* 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

Received November 22, 1999; revised April 28, 2000; accepted May 3, 2000

Thermocatalytic oxidation of dimethyl methylphosphonate (DMMP) was carried out on nickel, iron, copper, and vanadium oxides supported on γ -Al₂O₃. The vanadium catalyst was found to exhibit exceptional catalytic activity, even better than platinum catalysts. Varying the vanadium loading from 1 to 15% by weight indicated that 10% vanadium on Al₂O₃ was an optimal content. In conjunction with XRD patterns, monolayer dispersion of V₂O₅ on Al₂O₃ was considered to be beneficial to the longevity of these catalysts. Different supports, including Al₂O₃, SiO₂, and TiO₂, were examined and SiO₂ was the optimum support because of its large surface area and the ability to resist poisoning by P₂O₅. On 10% V/SiO₂ catalysts, 100% (to our limit of detection of 0.1%) conversion of DMMP was reached for more than 100 h at 723 K. IR, X-ray powder diffraction, ion chromatography, and XPS results illustrated that the used catalysts contained phosphorus species. The presence of methylphosphonic acid on the catalyst surface and downstream of the packed bed reactor demonstrated the difficulty of P-CH₃ cleavage. The deposition of coke in the catalyst bed and along the reactor wall resulted from the dehydration of methanol and DMMP on P₂O₅. Accumulation of phosphorus species and coke on catalysts gave rise to a tremendous loss of surface area. However, P₂O₅ itself was observed to catalyze the decomposition of DMMP. A mechanism for this reaction was proposed to explain these experimental observations. © 2000 Academic Press

INTRODUCTION

One of the most challenging problems currently faced on a virtually global scale is the disposal of immense stockpiles of outdated but highly hazardous military chemical weapons. The U.S. stockpile alone is estimated to consist of between 25,000 and 38,000 tons of various organophosphorus nerve agents and blistering agents (1, 2). The chemistry of chemical warfare agent (CWA) decomposition is thus an area of ongoing interest to the U.S. Army. In laboratory experiments, dimethyl methylphosphonate (DMMP) has been widely used as a simulant of CWAs because of its relative nontoxicity and similarity in chemical properties to CWAs.

¹ To whom correspondence should be addressed.

Although various methods, such as incineration (3), hydrolysis, stoichiometric reaction (4-9), and photodecomposition (10-12), have been applied for the disposal of CWAs, thermocatalytic oxidation is still an effective and cost-efficient method. Graven et al. (13) first studied the kinetic behavior of Pt/Al₂O₃ catalysts for the oxidation of organophosphonate compounds. Subsequently, Baier and Weller (14) investigated the deactivation of platinum catalysts. Complete conversion of toxic chemicals was reported during the "protection period," or "protection time," referred to as the period where 100% conversion is achieved. The catalyst then abruptly loses its activity after passing through the protection period. A possible explanation for catalyst deactivation is that the product H_3PO_4 (or P_2O_5) reacts with Al₂O₃ to give AlPO₄, which results in a weight increase and loss of surface area of the powder in the packed bed reactor. Similar observations were reported by Tzou and Weller (15), who also used platinized Al_2O_3 catalysts for the decomposition of DMMP. In this study, some by-products, such as dimethyl phosphate (DMP), monomethyl phosphate (MMP), monomethyl methylphosphonate (MMMP), and methylphosphonic acid (MPA), were identified:



To find less expensive materials to replace platinum catalysts, Lee *et al.* (16) developed Cu-substituted hydroxyapatite, which exhibited some interesting results. However, the catalytic activity shown on copper catalysts was still not as good as that on platinum catalysts despite partial recovery of activity by regeneration. In the studies of removal of some pollutants, including DMMP on nanoscale metal oxide particles, Jiang *et al.* (17) found a catalytic effect of first-row transition metal oxides coated on nanoscale CaO and MgO materials.

Mitchell *et al.* (18) systematically summarized the organophosphate surface chemistry conducted on various



transition metals, as well as metal oxides. Templeton and Weinberg (19, 20) investigated the behavior of DMMP on different substrates. DMMP adsorption involves P=O interaction with surface active sites. The methoxy group is then oxidized in the presence of oxygen and the strong $P-CH_3$ bond is expected to be broken at high temperatures.

Accumulation of P_2O_5 or other phosphorus species on catalyst surfaces leads to inevitable deactivation if the reaction proceeds below the sublimation point (623 K) of P_2O_5 . The reaction temperature thus must be controlled at high temperatures. Another reason ascribed to deactivation is the strong acidity of P_2O_5 , which is able to react with many metal oxides to form phosphonate compounds, especially for those that are basic. For the sake of practical use, new catalysts must possess specific properties including high activity, resistance against poisoning of phosphorus species, and low cost.

Herein are reported catalytic properties of nickel, copper, iron, and vanadium oxides for the destruction of DMMP. The effects of various supports (γ -Al₂O₃, SiO₂, and TiO₂) and reaction temperatures on protection times have been investigated. Characterization methods such as BET surface areas, Fourier transform infrared (FT-IR) X-ray powder diffraction (XRD), ion chromatography (IC), and XPS have been employed to study the deactivation of catalysts. Vanadium-based catalysts show excellent catalytic activity in this study.

EXPERIMENTAL

Apparatus

Evaluation of catalysts was carried out in a fixed-bed flow reactor with an inner diameter of 4 mm. Ultrahigh-purity air was used as a carrier gas at a flow rate of 50 mL/min and flowed through a bubbler filled with DMMP in order to create a vapor stream of DMMP. The concentration of DMMP at 298 K was 1300 ppm (1 Torr). A mass of 0.100 g of catalyst (28–48 mesh) was used for each test. The desired temperatures were controlled in a tubular furnace equipped with a temperature controller. Two gas chromatographs (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. Another GC equipped with a TCD and Carboxen column (Supelco) was used for detecting CO and CO_2 , which were decomposition products.

Catalyst Preparation

An impregnation method was employed to make catalysts. Precursors for the preparation of catalysts were Ni(NO₃)₂ · 6H₂O, Fe(NO₃)₂ · 9H₂O, Cu(NO₃)₂ · 2.5H₂O, NH₄VO₃, and Pt(acac)₂. The supports, γ -Al₂O₃, and amorphous SiO₂ and P-25 TiO₂ were obtained from Davidson

and Degussa, respectively. Salts were dissolved in distilled deionized water with the exception of Pt(acac)₂, which was dissolved in ethanol. Supports were then added to the solutions and stirred at room temperature for 12 h. Solutions were evaporated and dried at 393 K. Chunks of samples were ground and then calcined at 723 K for 6 h. Powdered samples were pelletized and sieved into 28- to 48-mesh granules for catalytic tests.

Characterization Methods

XRD experiments were carried out on a Scintag Model PDS 2000 diffractometer. Samples were loaded onto glass slides, and Cu*K* α radiation was used at 45 kV and 40 mA. The sample scans were collected between 5° and 80° 2 θ .

Diffuse reflectance FT-IR spectroscopy experiments were performed on a Nicolet 750 spectrometer with a mercury–cadmium–telluride (MCT) detector and KBr beam splitter. Spectra were collected with a resolution of 4 cm^{-1} using 100 scan averages.

Surface area measurements were obtained using the BET method with a Micromeritics ASAP 2010 apparatus. The samples were preheated at 423 K under vacuum before the measurement.

Aqueous extraction for ion chromatography analysis was performed 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 0.22- μ m filters. 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 Na₂CO₃ and 1.7 mM NaHCO₃, at an approximate pH of 10.

XPS data were obtained with a Physical Electronics Model 5400, ESCA System, equipped with a Mg anode, a hemispherical analyzer, a position sensitive detector, and an Omni-focus lens (nominal area diameters of 1.1 and 0.6 mm). All spectra were corrected for sample charging by referring the C 1s photoelectron line for adventitious carbon to 284.8 eV.

RESULTS

For comparison with results in the presence of catalysts, blank experiments with an empty reactor over the temperature range 573 to 723 K were carried out. The extent of DMMP oxidation at 723 K varied less than 2% when air with a flow rate of 50 mL/min passed through a saturator filled with DMMP to produce a vapor concentration of 1300 ppm (1 Torr). Therefore, it is reasonable to assume that no reaction takes place at temperatures lower than 723 K without a catalyst. In the following studies, the decomposition of DMMP under such conditions has been shown to be catalytic.



FIG. 1. Time course of DMMP conversion over different catalysts at 673 K. Inlet DMMP concentration, 1300 ppm; total flow rate: 50 mL/min.

Reactivity of Different Metal Oxide Catalysts Supported on γ -Al₂O₃

Figure 1 shows the time duration of DMMP conversion at 673 K over different metal oxides supported on γ -Al₂O₃. The loading contents of Ni, Fe, Cu, and V were 10% by weight. In this study, the 1 wt% Pt/Al₂O₃ catalyst was used for comparison since the catalyst was preferably tested for the decomposition of DMMP by several authors (13-16). Protection time (16), or protection period, defined as the period in which 100% conversion of DMMP is reached, is a very important parameter for the evaluation of a catalyst. The sequence of protection times obtained on these catalysts is as follows: $10\% \text{ V/Al}_2\text{O}_3$ (12.5 h) > 1% Pt/Al}2O_3 $(8.5 \ h) > 10\% \ Cu/Al_2O_3 \ (7.5 \ h) > Al_2O_3 \ (4.0 \ h) > 10\%$ Fe/Al_2O_3 (3.5 h) > 10% Ni/Al_2O_3 (1.5 h). Under our experimental conditions, the amounts of destroyed DMMP during the protection period are 20.18 and 2.42 mmol DMMP/g catalyst on 10% V/Al₂O₃ and 10% Ni/Al₂O₃ samples, respectively.

The vanadium catalyst exhibited higher catalytic activity than any other catalysts examined here. After passing the protection period, nickel, iron, and bare Al₂O₃ catalysts lost activity abruptly. The conversion of DMMP actually increased after 17 h on the 10% V/Al₂O₃ catalyst and is explained as follows. In our experiments, we observed the formation of significant amounts of coke initially on the catalyst bed and later along the reactor wall. We eventually discovered that the coke was generated via dehydration of methanol and DMMP on P₂O₅, a product from the decomposition of DMMP. Thus, the accumulated P₂O₅ along the reactor wall was able to catalyze the decomposition of DMMP to form coke. After passing through the protection period, P₂O₅ started to function as a catalyst, which led to the increase in conversion of DMMP (about 98%). The detailed role of P_2O_5 in this reaction will be discussed later. On the 10% V/Al₂O₃ catalyst, a "white fog" was observed to come out from the reactor with the flowing stream. The white fog was trapped with water for ion chromatography analysis (Table 2) and was found to primarily contain dissolved MPA.

Figure 1 shows that platinized Al_2O_3 , as a reference catalyst, is more active than copper, nickel, and iron catalysts, but not as active as vanadium catalysts. Lee *et al.* (16) reported that Cu-based catalysts revealed some unique properties, such as reduced need for regeneration. However, with respect to protection time, our studies show that Pt/Al_2O_3 was still superior to Cu-based systems. The protection time of 4 h obtained on bare γ -Al₂O₃ and DMMP. The protection times of nickel and iron catalysts were shorter than those on bare Al_2O_3 . The explanation for this observation is that bulk Al_2O_3 was covered by the phosphorus-poisoned iron, or nickel compounds (such as FePO₄, or Ni₃(PO₄)₂), which hindered the further exposure of Al₂O₃ to DMMP.

Figure 2 shows the variation of methanol concentrations in the flowing stream with reaction time. In general, we find that detection of methanol intermediates directly correlates with a decrease in DMMP conversion. Therefore, the trend shown in Fig. 2 is opposite to that in Fig. 1. The difference among these catalysts is that a small amount of methanol was observed on the vanadium catalyst, even during the protection period. After 15 h, the irregular change in methanol concentration on 10% V/Al₂O₃ is ascribed to catalytic effects of the formed P_2O_5 . On Al₂O₃, trace dimethyl ether (DME) was detected in the beginning of the reaction. The DME soon vanished with an increase in methanol.



FIG. 2. Methanol concentration as a function of time on stream. Reaction temperature, 673 K; inlet DMMP concentration, 1300 ppm; total flow rate, 50 mL/min.



FIG. 3. CO_2 concentration as a function of time on stream. Reaction temperature, 673 K; inlet DMMP concentration, 1300 ppm; total flow rate, 50 mL/min.

The CO₂ concentrations against reaction time are plotted in Fig. 3. The 1% Pt/Al₂O₃ catalyst exhibits large amounts of CO₂ production. During the protection period, an approximately 100% carbon balance estimated by the amounts of CO₂ and methanol was obtained only on the 1% Pt/Al₂O₃ catalyst, compared to all other catalysts tested. Note that the 10% V/Al₂O₃ catalyst, which showed the best conversion of DMMP, generated small amounts of CO₂. The carbon balance on this catalyst was about 10%, much less than 100%. The majority of carbon in DMMP was converted to coke deposited on the catalyst and downstream (along the reactor wall).

The Loading Concentration of Vanadium on Al₂O₃

Since the vanadium catalyst was found to be an excellent candidate for oxidation of DMMP, the effects of vanadium concentration on catalytic activity were investigated in order to find a catalyst with high activity and low metal loading. Figure 4 shows the protection times of vanadium catalysts with different loading content ranging from 1 to 15% by weight. The protection times on these catalysts were found to be 10% (12.5 h) > 5% (11.5 h) > 1% (9.5 h) > 15% (8 h). Compared to the 5% V/Al₂O₃ catalyst, the protection time of 10% V/Al₂O₃ increased by only 1 h although the content of vanadium was doubled. Furthermore, a short protection time was obtained on 15% V/Al₂O₃. This observation reveals that high loadings do not lead to more active catalysts. An interpretation of this trend is that high loading decreases the surface area (shown in Table 1), in particular, for the sample with loading content up to 15%. Pure V_2O_5 with a surface area of 1.6 m^2/g did not show activity since the protection time was less than half an hour.

Unlike the $10\% \text{ V/Al}_2\text{O}_3$ sample, no rebound in conversion of DMMP occurred on the 15, 5, and 1% vanadium



FIG. 4. Effects of vanadium loading on protection time. Reaction temperature, 673 K; inlet DMMP concentration, 1300 ppm; total flow rate, 50 mL/min.

catalysts. During the protection period, the product distribution of methanol on these four samples was very similar, approximately 50 ppm. The concentrations of CO_2 were 360, 250, 130, and 150 ppm on the 1, 5, 10, and 15% V/Al₂O₃ catalysts, respectively. Less than 10% of a carbon balance was obtained using these samples due to the formation of coke. The protection time using the 1% V/Al₂O₃ catalyst (9.5 h) was found to be 1 h longer than that for the 1% Pt/Al₂O₃ catalyst (8.5 h). In other words, the high activity and low loading levels for the vanadium catalyst indicate that these vanadium catalysts may be of practical interest for replacing platinum catalysts for the catalytic oxidation of DMMP.

TABLE 1

BET Surface Areas of Supports, Fresh Catalysts, and Used Catalysts

Catalysts	Surface areas of fresh catalysts (m²/g)	Surface areas of used catalysts (m²/g)	Reaction time (h)
SiO ₂	262.2		
TiO ₂	50.2		
V_2O_5	1.6		
Al_2O_3	289.2	3.8	5
10% Cu/Al ₂ O ₃	229.6	59.0	14
10% Fe/Al ₂ O ₃	223.8	136.8	5
10% Ni/Al ₂ O ₃	227.7	159.2	2
1% Pt/Al ₂ O ₃	284.8	13.2	14
1% V/Al ₂ O ₃	272.6	7.9	20
5% V/Al ₂ O ₃	255.9	11.2	50
10% V/Al ₂ O ₃	248.8	4.3	100
15% V/Al ₂ O ₃	203.8	16.5	20
10% V/TiO ₂	29.9	24.4	9
10% V/SiO ₂	190.4	10.6	100

Effects of Supports

The disadvantage of using γ -Al₂O₃ as a support is that basic γ -Al₂O₃ is able to react with acidic P₂O₅ to form AlPO₄. which can give rise to a drastic loss of surface area. For comparison, relatively acidic supports, such as SiO₂ and TiO₂, were chosen in this study. Figure 5 shows the conversion of DMMP on vanadium (10 wt%) catalysts supported on Al₂O₃, SiO₂, and TiO₂. XRD results (Fig. 8) demonstrated that SiO₂ was amorphous and that commercially available P-25 TiO₂ is a mixture of anatase and rutile with a ratio of 75:25 (21). The catalytic activity was markedly enhanced using SiO₂ for which a protection time of 25 h was obtained. This catalyst was actually run for 100 h. After passing through the protection time, the 10% V/SiO₂ catalyst deactivated slightly and the conversion of DMMP fluctuated between 99 and 100%. However, the 10% V/TiO₂ catalyst deactivated very quickly. The small surface area of this catalyst (29.9 m^2/g) may be the explanation for poor activity. Lee et al. (16) reported that Pt/TiO₂ was not as effective as Pt/Al₂O₃. The methanol concentrations were maintained at an average level of 50, 250, and 750 ppm on Al₂O₃, SiO₂, and TiO₂ catalysts, respectively. The CO₂ concentrations were 130 and 250 ppm on Al₂O₃ and SiO₂ catalysts, respectively. A trace amount of CO₂ was obtained on the TiO₂ catalyst. Pure SiO₂ and TiO₂ supports did not exhibit catalytic activity. Thus, in summary, 10% vanadium supported on SiO₂ was the best catalyst for the decomposition of DMMP.

Temperature Dependence

The oxidation of DMMP is a temperature-sensitive reaction because P_2O_5 , a decomposition product, has a high sublimation point (623 K). Low temperatures will therefore result in the accumulation of phosphorus species on



FIG. 5. Effects of supports on protection time. Reaction temperature, 673 K; inlet DMMP concentration, 1300 ppm; total flow rate, 50 mL/min.



FIG. 6. Temperature dependence of oxidative decomposition on 10% V/SiO₂. Inlet DMMP concentration, 1300 ppm; total flow rate, 50 mL/min.

catalyst surfaces. In order to investigate the effects of temperature on catalytic activity, temperature-dependent experiments were conducted on the 10% V/SiO₂ catalyst and these results are presented in Fig. 6. The protection times at 623, 673, and 723 K were 5, 25, and >100 h, respectively. At a temperature as low as 623 K, the coverage originated from the accumulation of phosphorus species on catalyst surfaces led to a drastic loss of active sites and surface area. This could be the main reason for the deactivation of the catalyst at such low temperatures. In contrast, the catalyst survived more than 100 h at 723 K. The concentration of CO₂ at 723 K was approximately 750 ppm. Small amounts of effluent methanol were detected (about 25 ppm). Coke was formed on the catalyst and along the reactor wall. In comparison, Graven et al. (13) examined the effect of temperature on deactivation over 0.5% Pt/Al₂O₃ catalysts and found that deactivation was still observed at 717 K under reaction conditions.

BET Surface Areas

The BET surface areas of fresh and used catalysts are listed in Table 1. All the used catalysts were run at 673 K for different times until they deactivated. The data for the 10% V/SiO₂ catalyst, which was tested at 723 K for 100 h, were not available because the catalyst was firmly stuck to the reactor wall and could not be removed. The bare Al₂O₃ lost its surface area very quickly (from 289 to $3.8 \text{ m}^2/\text{g in 5 h}$) because of the stoichiometric reaction between Al₂O₃ and DMMP. The large surface areas of the used 10% Cu/Al₂O₃ and 10% Fe/Al₂O₃ catalysts are due to their short reaction times related to their protection times (shown in Fig. 1). Investigation of the relationship between vanadium loading content and surface area indicates that increasing loading content (from 1 to 15%) gives rise to a decrease in surface area. After a 100-h run, both 10% V/Al₂O₃ and 10% V/SiO₂ samples lost almost all their surface area. The accumulation of phosphorus-bearing compounds and coke may be the explanation for this observation. A support with small surface area, such as TiO_2 , is not suitable for this reaction, in agreement with the reaction data shown in Fig. 5.

Fourier Transform Infrared Experiments

Investigation of the surface species on the catalysts before and after reaction was performed using FT-IR and the results are presented in Fig. 7. Spectrum A indicates that the fresh γ -Al₂O₃ contains large amounts of water. The broad band spanning the range of 3700–2500 cm⁻¹ is assigned to -OH stretches. Correspondingly, an -OH bend appears at 1643 cm⁻¹. An Al-O vibration is indicated by a broad band at 1036 cm⁻¹.

The deactivated Al₂O₃ shown in spectra B contains a P–CH₃ moiety (ν_a 3002 cm⁻¹; ν_s 2936 cm⁻¹; δ_a 1418 cm⁻¹; δ_s 1321 cm⁻¹), which has been explicitly illustrated by many authors (18–20, 22). The band at 1230 cm⁻¹ indicates the presence of P=O (23). Corbridge *et al.* (24) pointed out that the (P)–O–H stretch falls into two regions: 3000–2525 cm⁻¹ and 2400–2000 cm⁻¹. Three peaks appear at 2319, 2223, and 2106 cm⁻¹ and are assigned to a (P)–O–H stretch. Two bands with wavenumbers as high as 3832 and 3903 cm⁻¹ are difficult to assign and may be combination bands.



FIG. 7. Diffuse reflectance FT-IR spectra for fresh and used catalysts. (A) γ -Al₂O₃; (B) used γ -Al₂O₃; (C) 10% V/Al₂O₃; (D) used 10% V/Al₂O₃; (E) 10% V/SiO₂; (F) used 10% V/SiO₂.

Comparison of spectrum D (fresh 10% V/Al₂O₃ catalyst) and spectrum C (used catalyst) indicates the presence of P-CH₃, with two bands in the region of 3000-2900 cm^{-1} on the surface of the deactivated catalyst. In spectrum D, a striking band at 2345 cm^{-1} is due to the (P)-O-H stretch. Correspondingly, a (P)-O-H deformation appears at 1393 cm⁻¹. A weak adsorption at 1224 cm⁻¹ is due to a P=O stretch. Another significant difference between spectra C and D is the disappearance of an Al-O vibration near 1036 cm⁻¹. This observation demonstrates that the poisoning of γ -Al₂O₃ by phosphorus species resulted in a structural change of Al₂O₃. Because of destruction of the hydrophilic surface of γ -Al₂O₃, the deactivated sample no longer contains physisorbed water, which is illustrated by the disappearance of the -OH vibration (stretch in the range 3700-2500 cm⁻¹ and bend at 1643 cm⁻¹). In contrast, the SiO₂ surface is resistant against poisoning of phosphorus-containing compounds. No obvious (P)-O-H band was observed despite the presence of trace P-CH₃ moieties. However, the surface still lost water and free (Si)-O-H groups (3747 cm⁻¹). Phosphorus-bearing compounds were invisible on the used 10% V/TiO₂ catalyst. This could be due to the short testing time (8 h).

X-Ray Diffraction Patterns

XRD patterns for different samples are shown in Fig. 8. The characteristic indices of crystalline V₂O₅ were observed over 10 and 15% V/Al₂O₃ catalysts (patterns C and D). In particular, bulk V_2O_5 was obviously present on the 15% V/Al₂O₃ catalyst. However, no such characteristic indices were observed if the loading content of V₂O₅ was lower than 5%. It is reasonable to assume that V_2O_5 is dispersed on Al₂O₃ as a monolayer. On amorphous SiO₂ with a surface area of 262.2 m^2/g , a small amount of bulk V₂O₅ was observed. Two types of TiO₂ crystallinity, anatase and rutile, as well as V_2O_5 were presented on the 10% V/TiO₂ catalyst. Comparison of the used and fresh catalysts indicates that a phase transformation occurred on the used 10% V/Al₂O₃ catalyst (pattern E). The broad peak with a d-spacing of 4.23 is probably due to the formation of noncrystalline AlPO₄. The intensity of the characteristic indices of γ -Al₂O₃ decreased. The results are in good agreement with a report by Baier and Weller (14). In combination with BET results, we believe that the formation of AlPO₄ is the reason for the decrease in surface area of the used Al₂O₃ systems.

Ion Chromatography Results

Ion chromatography was used to analyze the contents of PO_4^{3-} , methyl phosphonic acid (MPA), and methyl methylphosphonate (MMP) on different samples. Samples were extracted with water prior to analysis. Thus, only water-soluble species could be detected using this method. However, DMMP was undetectable because of its low conductivity in water. Table 2 reveals that the used 10% V/SiO₂



FIG. 8. X-ray patterns for different vanadium catalysts. (A) 1% V/Al₂O₃; (B) 5% V/Al₂O₃; (C) 10% V/Al₂O₃; (D) 15% V/Al₂O₃; (E) used 10% V/Al₂O₃; (F) 10% V/SiO₂; (G) 10% V/TiO₂.

catalyst contained more PO_4^{3-} than the 10% V/Al₂O₃ catalyst despite the same reaction time (100 h) and reaction temperature (673 K). This is due to the presence of AlPO₄, which is insoluble in water and thus cannot be measured. The coke scraped from the reactor wall contained a large amount of PO_4^{3-} , probably originated from the hydrolysis of P_2O_5 , as well as trace MMP without quantitative results. The white fog coming from the outlet of the reactor was collected for 50 h using distilled water. PO_4^{3-} , MPA, and trace MMP were detected. Compared with PO_4^{3-} , MPA was

TABLE 2

Content of Phosphorus Species on Different Samples

Sample	PO_4^{3-}	MPA	MMP
10% V/Al ₂ O ₃	20.09 (mg/g)	2.97 (mg/g)	None
10% V/SiO ₂	118.07 (mg/g)	4.62 (mg/g)	None
Coke	184.26 (mg/g)	3.51 (mg/g)	Small amount
White fog	15.72 (ppm)	457.48 (ppm)	Small amount



FIG. 9. XPS spectrum of the used 10% V/SiO₂ catalyst (100 h).

present in large amounts because of the volatility of MPA. This is additional evidence of the difficulty in cleavage of $P-CH_3$ bonds.

XPS Spectra

XPS spectra for the used $10\% \text{ V/SiO}_2$ materials are shown in Fig. 9. The binding energies for specific elements are labeled on the corresponding peaks. In comparison to the fresh catalyst, the used catalyst obviously contains two new elements: phosphorus and carbon, which are illustrated by the binding energies of 134.2 eV for P 2*p* and 284.8 eV for C 1*s*. The binding energy for phosphorus indicates that phosphorus is mostly in the form of PO₄³⁻. This is in good agreement with IC results. The binding energy for carbon matches that for graphitic carbon (25). The surface concentrations (at.%) of the used catalyst are 65.6% (O), 1.0% (V), 5.5% (P), 18.2% (P), and 9.7% (Si).

DISCUSSION

Catalytic Properties of Different Catalysts

A significant challenge arising from the catalytic oxidation of DMMP is the deactivation of catalysts. The deactivation is primarily due to phosphorus species reacting with active components or supports. In our studies, four types of supported metal oxides were examined. Nickel, iron, and copper catalysts were not able to survive long-time operation. The main reason is that the metal oxides, NiO, Fe₂O₃, and CuO, as well as the Al₂O₃ support,

can react with the by-product, P_2O_5 or H_3PO_4 , to form stable phosphates, such as $Ni_3(PO_4)_2$, FePO₄, Cu₃(PO₄)₂, and AlPO₄. A weight increase of approximately 20% was observed on the majority of these catalysts. In contrast, vanadium phosphate is hard to form because of the weak acidity of V_2O_5 . In industry, supported vanadia is currently employed to replace platinum catalysts for the conversion of sulfur dioxide to sulfur trioxide in the manufacture of sulfuric acid (26). The resistance of V_2O_5 against poisoning of strong anhydrides, for instance, SO₃ and P₂O₅, provides potential catalytic ability for the decomposition of DMMP. Our experimental results reveal that vanadium catalysts exhibit exceptional activity, even better than platinum catalysts. Jiang et al. (17) also reported a catalytic effect of V₂O₅ for the destruction of chlorocarbons, organophosphorus compounds, and acid gases.

The studies of loading content on Al₂O₃ indicate the necessity of appropriate vanadium content for maintaining high activity. In combination with XRD patterns and reaction results (Fig. 4), 10% V/Al₂O₃ exhibited the longest protection time when the loading content is varied from 1 to 15%. XRD results indicate that the V_2O_5 is dispersed on Al_2O_3 as a monolayer if vanadium content is lower than 5%. High loading content, such as 15%, decreases the protection time due to the appearance of bulk V₂O₅, which shows very poor activity. However, samples with low loading content, for instance, 1%, do not exhibit a long protection time because fewer active sites are available for reaction. Thus, monolayer dispersion with a vanadium mass of 5-10 wt% on supports appears to be optimum for high catalytic activity. Moreover, high loading inevitably gives rise to small surface area, which is another factor influencing the catalytic activity.

There are two requirements for catalyst supports: ability to resist poisoning of phosphorus species and providing surface area for the dispersion of active components. Although γ -Al₂O₃ has a large surface area, 289.2 m²/g, it is not resistant to the poisoning of acidic P_2O_5 . During the course of the reaction, the formation of AlPO₄ led to the collapse of crystalline γ -Al₂O₃ (14). On the other hand, although TiO₂ is inert to P₂O₅ poisoning, the low surface area $(50.2 \text{ m}^2/\text{g})$ inherently limits the catalytic activity. In practical use, neither of these two supports is suitable for catalyst preparation. In contrast, SiO₂ appears to meet the two requirements described above. The large surface area $(262.2 \text{ m}^2/\text{g})$ and inert chemical properties to P₂O₅ make SiO₂ an excellent support for V₂O₅ dispersion. Thus, the 10% V/SiO₂ catalyst exhibits exceptional activity for the catalytic decomposition of DMMP.

Temperature is also a very important factor that affects the protection time. High temperature can enhance the destruction of DMMP. Because of the high sublimation point of P_2O_5 (623 K), theoretically, the reaction temperature must be kept higher than 623 K in order to avoid the condensation of P_2O_5 on catalyst surfaces. The strong effects of reaction temperature on protection times are illustrated in Fig. 6. No effluent DMMP was detected at 723 K on 10% V/SiO₂ even though the catalyst was run for 100 h. However, IC results indicate that there are still large amounts of PO_4^{3-} and a small amount of MPA deposited on the used 10% V/SiO₂ catalysts at the operating temperature of 673 K. Consequently, it is very difficult to keep the catalyst free of phosphorus species at 673 K.

IR and IC results indicate the presence of MPA on the used catalysts. Templeton and Weinberg (19) have reported that DMMP is adsorbed dissociatively on Al₂O₃ surfaces at temperatures above 295 K. Surface temperatures above 473 K led to the dealkylation of adsorbed species, resulting in the formation of adsorbed MPA. The MPA is expected to decompose further only above 1023 K. Similarly, Mitchell et al. [18] have reported that MPA with intact P-CH₃ bonds is resistant to further oxidation even in the presence of oxygen at 573–673 K on aluminum, magnesium, and lanthanum oxides. Our experimental results are consistent with those reports. Table 2 illustrates that the exhaust gases and the liquid condensates in the low-temperature zone in the reactor contain MPA. The P-CH₃ moiety is hard to cleave even though the majority of DMMP is decomposed into phosphorus oxide or phosphate. Thus, the suggested scheme for the process of DMMP decomposition is: $DMMP \rightarrow MMP \rightarrow MPA \rightarrow PA$ (phosphoric acid). At high temperature, phosphoric acid may exist as P₂O₅ as a result of dehydration.

Role of P₂O₅ for DMMP Decomposition

The carbon balance determined by summation of CO_2 and methanol was about 30%, much less than 100%, as expected due to the large amount of coke mixed with P_2O_5 (or other phosphorus species) deposited on the catalyst bed and along the reactor wall. After the 10% V/SiO₂ catalyst (Fig. 6) was operated at 673 K for 50 h, the catalyst was removed from the reactor but the deposited coke and P_2O_5 remained strongly adhered to the reactor walls. Surprisingly, a conversion of DMMP as high as 98% was reached using the deposited coke and P_2O_5 as a catalyst. In other words, either coke or P_2O_5 behaved as a catalyst in this case. In our study, we believe that P_2O_5 itself can catalyze the decomposition of DMMP. The following scheme [1]–[4] is suggested to explain the reaction processes:

$$DMMP + O_2 \xrightarrow{Catalyst} Methanol + CO_2 + P_2O_5$$
[1]

$$P_2O_5 + Metal Oxide \rightarrow Phosphate$$
 [2]

$$DMMP + O_2 \xrightarrow{P_2O_5} Methanol + CO_2 + Coke + P_2O_5 \quad [3]$$

D.O

$$Methanol \xrightarrow{1_2O_5} Coke + CO_2$$
 [4]

In the beginning of the reaction, DMMP is catalytically converted to methanol, CO_2 , and P_2O_5 in the presence of

oxygen (Step 1). Subsequently, P_2O_5 can react with metal oxides to form phosphates (Step 2). If more P_2O_5 is accumulated on the catalyst or condensed along the reactor wall, it is able to catalyze the decomposition of DMMP to form new P_2O_5 and other products (Step 3) since P_2O_5 is a strong desiccant and is able to extract water even from organic compounds. The assumptions have been confirmed by the following experiments:

Experiment 1. More than 90% conversion of DMMP was obtained at 673 K when an air stream with DMMP vapor passed through the pure P_2O_5 bed in the absence of any aforementioned catalysts. P_2O_5 sublimed slowly and then condensed on the downstream reactor wall. Coke was observed as the major product and formed in the region of P_2O_5 . Methanol and CO_2 were present in small amounts.

Experiment 2. If the carrier gas (air) was replaced with helium, high conversion of DMMP (\sim 90%) and coke was still obtained on P₂O₅. Instead of CO₂, dimethyl ether and methanol were observed.

Experiment 3. Coke was formed at 673 K on P_2O_5 if DMMP was replaced with methanol vapor.

Experiments 1 and 3 verify the appropriateness of Steps 3 and 4, respectively. Experiment 2 demonstrates that P_2O_5 can remove molecular water from DMMP without the assistance of oxygen. However, the detection of CO₂ and methanol, instead of dimethyl ether, in the oxidation of DMMP demonstrates that the key reaction proceeds via Step 3 after P₂O₅ starts to function as a catalyst. Over vanadium catalysts, for instance, 10% V/SiO₂ catalyst, the reaction proceeds as in Step 1. P₂O₅ accumulates in the catalyst bed at the start of DMMP decomposition since V₂O₅ and SiO₂ are resistant to P_2O_5 . After the vanadium catalyst passes the protection period, Step 3 actually dominates the reaction because the accumulated P₂O₅ begins to catalyze the oxidation of DMMP. The conversion of DMMP at this stage is not absolutely 100% (99-100%; Fig. 6). The prerequisite for Step 3 is adequate accumulation of P₂O₅. Therefore, the long protection time shown on $10\% \text{ V/Al}_2\text{O}_3$ and 10% V/SiO₂ catalysts is due to the combination of the original vanadium catalysts and subsequent P2O5. However, on other metal oxides (NiO, Fe₂O₃, and CuO) as well as Al₂O₃ supported catalysts, the combining effects of both catalysts and P_2O_5 is disrupted because of consumption of P_2O_5 in Step 2. Insufficient P_2O_5 is generated during the protection period for subsequent DMMP decomposition. This conclusion can be used to interpret the data for the $10\% \text{ V/Al}_2\text{O}_3$ catalyst in Fig. 1. If a catalyst cannot survive for a sufficient time to provide enough P₂O₅, the conversion of DMMP will abruptly decrease after the protection time. The unusual behavior of the 10% V/SiO₂ catalyst is due to the resistance of both the active component (V_2O_5) and the support (SiO_2) against the poisoning of P_2O_5 . Therefore, P_2O_5 plays two totally different roles for different catalysts: (i) P_2O_5 can

poison catalysts to form phosphates if the active components or supports are able to react with acidic P_2O_5 and (ii) instead, P_2O_5 can assist to decompose DMMP if a certain amount of P_2O_5 is accumulated in a reactor. Detailed studies of dehydration of DMMP on P_2O_5 are still under investigation.

CONCLUSIONS

(1) In comparison with nickel, iron, and copper catalysts, the vanadium catalyst exhibited exceptional catalytic activity for the decomposition of DMMP. The $1\% \text{ V/Al}_2\text{O}_3$ catalyst was superior to the $1\% \text{ Pt/Al}_2\text{O}_3$ catalyst.

(2) Monolayer dispersion of vanadia on supports was beneficial to catalytic activity. The appearance of bulk vanadia unfavorably reduced the protection time.

(3) Amorphous SiO₂ with a large surface area and inert chemical properties to P_2O_5 is a good support for the dispersion of active components. In this study, 10% V/SiO₂ catalyst displayed the longest protection time under comparable conditions. The occurrence of deactivation over Al_2O_3 supported catalysts is due to the formation of noncrystalline $AlPO_4$ and the deposition of coke, which resulted in the loss of surface area.

(4) The P-CH₃ moiety detected by IR and IC is hard to cleave. The process of DMMP decomposition is as follows: DMMP \rightarrow MMP \rightarrow MP \rightarrow PA.

(5) P_2O_5 generated from the DMMP decomposition was able to catalyze DMMP decomposition to form coke. Therefore, P_2O_5 contributed to DMMP decomposition after the catalyst passed through the protection period.

(6) The oxidation of DMMP is highly temperature dependent. At 723 K, 10% V/SiO₂ catalysts exhibited more than 100 h of protection time. Hence, under such operating conditions, the catalyst could be practically used for the destruction of chemical warfare agents.

ACKNOWLEDGMENTS

We thank the U.S. Army and United Technologies Research Center, East Hartford, Connecticut, for support of this work. This work was supported by the U.S. Army Research Office, as a subcontract to UTRC under DAAH04-96-C-0067.

REFERENCES

- Adam, R. E., "Chemical Warfare, Chemical Disarmament." Indiana Univ. Press, Bloomington, 1990.
- Ekerdt, J. G., Klabunde, K. J., Shapley, J. R., White, J. M., and Yates, J. T., Jr., J. Phys. Chem. 92, 6182 (1998).
- National Research Council, "Review and Evaluation of Alternative Chemical Disposal Technologies." National Academy Press, Washington, DC, 1996.
- 4. Gustafson, R. L., and Martell, A. E., J. Am. Chem. Soc. 84, 2309 (1962).
- 5. Epstein, J., Callahan, J. J., and Bauer, V. E., Phosphorus 4, 157 (1974).
- 6. Lin, S. T., and Klabunde, K. J., Langmuir 1, 600 (1985).
- 7. Li, Y. X., and Klabunde, K. J., Langmuir 7, 1388 (1991).

- 8. Yang, Y.-C., Baker, J. A., and Ward, J. R., Chem. Rev. 92, 1729 (1992).
- 9. Yang, Y.-C., Acc. Chem. Res. 32, 109 (1999).
- Segal, S. R., Suib, S. L., Tang, X., and Satyapal, S., Chem. Mater. 11, 1687 (1999).
- O'Shea, K. E., Beightol, S., Garcia, I., Aguilar, M., Kalen, D. V., and Copper, W. J., J. Photochem. Photobiol. A Chem. 107, 221 (1997).
- 12. Nakamura, M., Shi, M., Okamoto, Y., and Takamuku, S., J. Photochem. Photobiol. A Chem. 85, 111 (1995).
- Graven, W. M., Weller, S. W., and Peters, D. L., *Ind. Eng. Chem. Process Des. Dev.* 5, 183 (1966).
- 14. Baier, R. W., and Weller, S. W., *Ind. Eng. Chem. Proc. Des. Dev.* 6, 380 (1967).
- 15. Tzou, T. Z., and Weller, S. W., J. Catal. 146, 370 (1994).
- Lee, K. Y., Houalla, M., Hercules, D. M., and Hall, W. K., J. Catal. 145, 223 (1994).
- 17. Jiang, Y., Decker, S., Mohs, C., and Klabunde, K. J., *J. Catal.* **180**, 24 (1998).

- Mitchell, M. B., Sheinker, V. N., and Mintz, E. A., J. Phys. Chem. B 101, 11192 (1997).
- Templeton, M. K., and Weinberg, W. H., J. Am. Chem. Soc. 107, 97 (1985).
- Templeton, M. K., and Weinberg, W. H., J. Am. Chem. Soc. 107, 774 (1985).
- 21. Fox, M. A., and Dulay, M. T., Chem. Rev. 93, 341 (1993).
- Li, Y.-X., Schlup, J. R., and Klabunde, K. J., *Langmuir* 7, 1394 (1991).
- Thomas, L. C., and Chittenden, R. A., Spetrochim. Acta 20, 467 (1964).
- Corbridge, D. E. C., Grayson, M., and Griffith, E. J. (Eds.), *in* "Topics in Phosphorus Chemistry," Vol. 5, p. 275. Interscience, New York, 1969.
- Moulder, J. F., Stickle, W. F., Sobol, P. E., and Bomben, K. D., "Handbook of X-ray Photoelectron Spectroscopy" (J. Chastain, Ed.). Perkin–Elmer, Eden Prairie, MN, 1992.
- 26. Gameron, G. M., Chem. Eng. Prog. 78, 71 (1982).