JOURNAL OF CATALYSIS **145**, 223–231 (1994)

Catalytic Oxidative Decomposition of Dimethyl Methylphosphonate over Cu-Substituted Hydroxyapatite

Kwan Young Lee,[1] Marwan Houalla, David M. Hercules, and W. Keith Hall[2]

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received April 19, 1993; revised August 16, 1993

The oxidative decomposition of dimethyl methylphosphonate (DMMP) has been studied over Cu-substituted hydroxyapatite catalysts in a flow reactor in the temperature range 373–773 K. By substitution of a portion of the Ca^{2+} by Cu^{2+} in the hydroxyapatite lattice, the catalytic activity was markedly increased. The composition $Cu_2Ca_8(PO_4)_6(OH)_2$, herein called Cu2-HA, had the highest activity among these catalysts. All the catalysts showed 100% conversion at the beginning of the reaction, but became deactivated after a period of time. Only CO_2 and H_2O were produced during the "protection period" of the 100% conversion. With deactivation, CO_2 formation decreased and methanol and dimethyl ether appeared as products. A phosphorus-containing product was not detected in the gas phase. Some condensate of phosphoric acid appeared in the outlet of the reactor after deactivation. Several analytical methods revealed that carbonaceous compounds did not remain on the surface after 773-K oxidative regeneration, but the phosphorus compounds that had accumulated during the reaction were not eliminated. The catalytic activity of Cu-substituted hydroxyapatite was compared to that of conventional supported Pt catalysts. This study suggested that easily made and cheap Cu-substituted hydroxyapatite catalysts could be used as successful alternatives to conventional adsorbents and catalytic systems based on supported noble metals devised for protection against nerve gases in warfare.

INTRODUCTION

There is renewed interest in developing reliable methods to transform toxic agents into harmless substances for defense against chemical warfare, as well as for atmospheric pollution abatement. Such catalysts would be useful for the destruction of certain insecticides and other volatile organic compounds (VOC). Several recent studies using dimethyl methylphosphonate [$CH_3(CH_3O)_2PO$, DMMP] as a simulant gas have concentrated on the surface chemistry (1–9). The catalytic reactions, however, have not yet been widely investigated.

Pt/Al_2O_3 was first reported by Weller and coworkers (10, 11) as an oxidation catalyst for DMMP and for isopropyl methylphosphonofluoridate (Sarin or GB). A fresh catalyst completely converted DMMP even at a low temperature (473 K) in a conventional flow system. However, after a certain time on stream, the catalyst abruptly lost activity. The major products were CH_3OH, CO_2, and H_2O. The reaction over the deactivated catalyst was principally hydrolysis to give methanol and phosphoric acid which was obtained as a syrupy condensate at the exit of the reactor. A typical behavior pattern observed regardless of the reaction temperatures is shown as Fig. 1. It consists of a "protection period" (A) where we report that only CO_2 and H_2O were formed, then a sharp deactivation period (B) where CH_3OH was released from the catalyst, and finally a poisoned catalyst (C) which mainly released CH_3OH. Much of the paper of Graven *et al.* (10) is devoted to the uncatalyzed reaction and to the "Steady-State Kinetics" determined in region C of Fig. 1. For practical use the length of the protection period (region A) is critical. However, regions B and C must be considered from the viewpoint of the nature of the poisoning and the possibility of regeneration of the catalyst.

In their review paper (1), Ekerdt *et al.* stated, "The reasons for selecting a Pt catalyst are not detailed in the existing literature, ..." Actually Graven *et al.* (10) stated explicitly, "A considerable number of catalysts, both commercial and laboratory-prepared, were initially screened. Platinum supported on high area alumina gave the most promising results. . . . " However, Graven *et al.* did not list the catalysts evaluated, nor did they provide data to permit a comparison to be made between a typical commercial supported Pt catalyst and those others screened. In a later paper Baier and Weller (11) reported the initial products from GB (region A) were stoichiometric amounts of CO_2, H_2O, HF, and H_3PO_4, but that in the lined-out condition the reaction shifted to dealkylation producing fluor acid and C_3H_6.

Among the model surface chemistry studies, Mo(110) was reported by Yates and co-workers to show the best

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[1] On leave from the University of Tokyo, Dept. of Synthetic Chemistry.

[2] To whom correspondence should be addressed.

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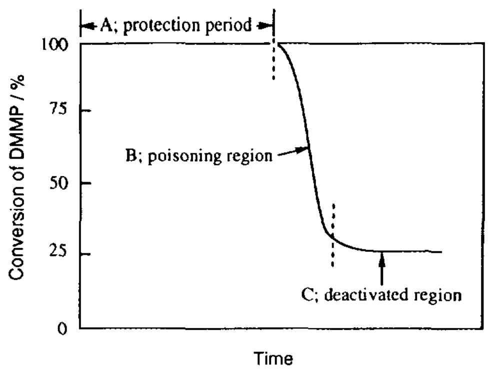


FIG. 1. Typical behavior of oxidative decomposition of DMMP over Pt/Al_2O_3.

performance for DMMP decomposition (6–8). When a 1:2 $DMMP/O_2$ flux [DMMP: 3.4×10^{13} molecules/($cm^2 \cdot min$)] was incident on a Mo(110) disk at a temperature of 898 K, carbon monoxide and phosphorus oxide were produced steadily and only oxygen was present in measurable concentrations on the surface. The authors claimed "This is the first report of the sustained catalytic destruction of DMMP." Ni(111) and Pd(111) single crystals were investigated but the activities were lower than that of Mo(110) (1–8). Unfortunately, Pt was not investigated. Supported Mo metal cannot exist under the oxidizing conditions required for practical application. Molybdena–alumina catalysts, on the other hand, can be used for this purpose, but tests made in the present work showed that CO was produced rather than CO_2 as a major product, *vide infra*.

More recently, Hsu *et al.* (9a) investigated the oxidation of DMMP over monolithic Pt/TiO_2/cordierite catalyst and continuously monitored the exit gas with an on-line mass spectrometer. Under low-pressure conditions (total pressure, 0.04–0.1 Torr; 1% DMMP and 10% O_2 in He), DMMP was converted to CO_2 and H_2O at 523 K without the appearance of phosphorus containing products. In a comparison with a three-way pelleted NO_x catalyst, the monolithic catalyst showed superior performance characteristics in terms of operating temperature, DMMP destruction efficiency, and reaction products. Results of spectroscopic surface analysis revealed the formation of P_2O_5 on catalyst surfaces. Further work (9b) showed that Pt/TiO_2 was superior to Pt/Al_2O_3 for protection against a variety of lethal gases.

Although these previous studies indicated that their catalysts were superior for the complete construction of DMMP, a direct comparison in the conventional flow system under the same operating conditions was not reported. Therefore, in the present work a comparison was made among those catalysts and with another candidate, viz., Cu-substituted hydroxyapatites.

In considering a new catalytic system for this reaction, both its activity and its resistance to poisoning are important factors. The oxidative decomposition of organophosphorus compounds as expressed in Eq. [1] leads to the production of phosphorous acids and oxides that are retained by the catalyst, i.e.,

$$CH_3(CH_3O)_2PO + (x + 15)/2O_2 = 3CO_2 + 9/2H_2O + PO_x \qquad [1]$$

(or H_3PO_4 from the reaction of H_2O with PO_x).

When DMMP is completely oxidized as in Eq. [1] at temperatures below 623 K, the PO_x is not removed from the surface. The sublimation point of P_2O_5 is 633 K. Thus at low temperatures catalyst poisoning may be unavoidable.

A satisfactory system which must operate at low temperatures should have the following properties: (i) The catalyst must have a high activity for the complete combustion of DMMP in air; (ii) since PO_x formed during the reaction is also toxic, retention by the catalyst may be desirable; and (iii) the deactivated catalyst should be easily regenerated or, when regeneration is not possible, discarded safely at minimum cost. The cost of Cu2-HA prepared in tonnage quantities may be estimated at several dollars per pound. The cost of the Cu/pound of catalyst is currently about 12 cents. It could be discarded without environmental impact. By contrast, Pt is presently valued in excess of $400/oz. A pound of alumina with 2% Pt would contain around $80 worth of Pt. True, in principle, most of this is recoverable, but in warfare this may not be practical. On the basis of this general idea, hydroxyapatite, a kind of calcium phosphate of variable composition, was selected in this study. Since hydroxyapatite has a phosphate lattice, and H_2O is produced as well (Eq. [1]), the possibility existed that this deposit could become incorporated into or extend the lattice.

Hydroxyapatites have several unique characteristics, which make them worthy of consideration as catalysts. The chemical composition can be varied from the stoichiometric form (Ca/P = 1.67) to calcium-deficient forms (nearly that of tricalcium phosphate, Ca/P = 1.5) (12–14) without any significant change in the apatite structure. The calcium-deficient hydroxyapatites function as acid catalysts (15–21), while stoichiometric hydroxyapatite has basic properties (22). The selectivity of alcohol dehydrogenation and dehydration over hydroxyapatite catalyst has been reported to be controlled by this stoichiometry (23). Hydroxyapatites can be prepared cheaply from readily available materials. They have relatively high surface areas, 60–100 m^2/g, and high heat resistance (stable up to 1173 K) due to their nonporous structures (15). One more important feature of this material is cation and anion exchangeability (24, 25). The cation exchangeability can endow redox activity to the hydroxyapatite, even though, surprisingly, no oxidation system using the hydroxyapatite catalyst has so far been studied. These many advantages make the hydroxyapatites attractive as catalysts for nerve gas decomposition. This study focuses on the feasibility of their use as practical nerve gas decomposition catalysts.

EXPERIMENTAL

Catalyst Preparation

Calcium hydroxyapatites (stoichiometric and deficient forms) were made as described previously (15). The volume of H_3PO_4 (Fisher) required to give a desired Ca/P ratio was slowly titrated while stirring into the $Ca(OH)_2$ solution at room temperature. Pyrex vessels were used and the reagents were mixed under N_2 to minimize reaction with atmospheric CO_2. A fine gel-like precipitate appeared immediately, and this suspension was heated for 15 h at 353 K for aging and crystallization. The slurry was then filtered and dried at 403 K for another 15 h. The products, white crystalline solids, were sieved for catalytic studies to 40–80 mesh. The $Ca(OH)_2$ solution was prepared by dissolving CaO obtained by decomposition of $CaCO_3$ in vacuum at 1173 K, in doubly distilled water. Saturated $Ca(OH)_2$ solution was filtered and used after determination of the Ca concentration by atomic absorption.

Cu-substituted hydroxyapatites were obtained by coprecipitation using calcium nitrate (Sigma, $Ca(NO_3)_2 \cdot 4H_2O$) and copper nitrate (Sigma, $Cu(NO_3)_2 \cdot 2.5H_2O$) mixed solution [total concentration (Cu + Ca): 0.25 *M*] and a diammonium hydrogen phosphate (Sigma, $(NH_4)_2HPO_4$) solution (0.25 *M*) according to the procedure of Pujari and Patel (25). Doubly distilled water was used. The pH of each solution was adjusted to pH > 11 by addition of aqueous ammonia and precipitation was carried out under anaerobic conditions. The precipitate and mother liquor were aged by boiling under reflux for 6 h.

Pt-supported γ-Al_2O_3 (Ketjen), TiO_2 (Degussa), and hydroxyapatite (Aldrich) were prepared by adding the supports into a solution of platinum acetylacetonate in methylethylketone and ethanol (1 : 1). Butanol was then added to precipitate the platinum acetylacetonate onto the surface of the support. This was followed by heating to 573 K to decompose the acetylacetonate. The resulting powder was pressed into a soft pellet and then crushed to obtain the 40–80 mesh fraction. Mo supported on γ-Al_2O_3, TiO_2, and hydroxyapatite catalysts were made by the incipient wetness method using ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Aldrich] and similarly treated.

Techniques

X-ray diffraction. X-ray diffraction patterns of the samples were obtained with Diano XRD-700 powder diffractometer using Cu $K\alpha$ radiation (1.54056 Å). The X-ray tube was operated at 50 kV and 25 mA. Spectra were scanned at a rate of 0.2° min^{-1} (in 2θ).

ESCA. ESCA spectra were recorded with an AEI ES200 A spectrometer equipped with an aluminum anode (Al $K\alpha$ = 1486.6 eV) operated at 12 kV and 20 mA. The residual pressure inside the analysis chamber was typically 5×10^{-8} Torr. The $Ca2p_{3/2}$ line (347.5 eV) of the hydroxyapatite was used as a reference for ESCA binding energy measurements.

MAS NMR spectra. MAS NMR spectra of the ^{31}P nuclei were recorded using a Bruker MSL-300 spectrometer at 121.497 MHz with a spinning rate of 5 kHz. The chemical shifts were obtained relative to 85% H_3PO_4 as a standard.

Infrared spectra. Infrared spectra were recorded at room temperature on a Cygnus 100 FT-IR spectrometer (Mattson, Inc.) at a resolution of 4 cm^{-1}. The infrared cell has been described previously (26). It had a built-in furnace which could be used to pretreat samples *in situ* at high temperatures. Samples were mounted in the cell as wafers having a thickness between 10 and 20 mg/cm^2.

Microbalance Experiments

Microbalance experiments were made with a Cahn Model RG balance in the flow mode. Weight changes with time were recorded under the same conditions used for the catalytic reaction.

Catalytic Reactions

Catalytic reactions were studied in a conventional flow system. 0.3 g of catalyst (40–80 mesh) was packed between quartz wool plugs in an 8-mm quartz tube reactor and N_2 was used as a carrier gas of DMMP. This was saturated with DMMP at 298 K at a flow rate of 60 ml/min and was mixed with an equimolar mixture of O_2 and N_2 (20 ml/min each) just before the inlet of the reactor. This mixture was passed over the catalysts at atmospheric pressure. The total flow rate was thus 100 ml/min and the final O_2/N_2 ratio was 1/4. Hence the DMMP concentration at the inlet was 2.885×10^{-5} mol/liter (NTP). The flow rates were maintained constant by rotameters and metering values. These conditions were maintained at all temperatures and in all experiments. All the lines from the saturator were heated to 393 K to prevent condensation of DMMP. The catalyst was pretreated at 773 K for 1 h with flowing N_2 before reaction. The conversion of DMMP was determined by the disappearance of the reactant and the products were analyzed by GC (Gow-Mac, GC-750). CH_3OH, CH_3OCH_3, and DMMP were separated over 10% Carbowax 20M on Supelcoport column (Supelco, 2 m × 1/8″ O.D.) at 368 K; detection was by FID. CO_2, CO, O_2, and N_2 were separated by CTR column (Alltech) at 303 K and detected by TCD. The temperatures were controlled to ±0.5 K.

RESULTS

Reactivity of Cu-Substituted Hydroxyapatite Catalyst

Figure 2 shows the XRD patterns of the Cu-substituted hydroxyapatites [$Cu_xCa_{10-x}(PO_4)_6(OH)_2$, which is abbreviated to Cu*X*-HA] from 20° to 60° in 2θ. Only the XRD pattern characteristic of the apatite structure was observed up to Cu2-HA where the pattern became diffuse. For $X > 2$ additional lines were observed that could be assigned to $Cu_2(OH)PO_4$.

The time courses of the DMMP conversion at 573 K over hydroxyapatites (stoichiometric and Ca-deficient) and the Cu-substituted ones (Cu0.25-HA and Cu2-HA) are shown in Fig. 3. In the protection period, 100% conversion of DMMP was observed for all catalysts. In this region, the only products detected were CO_2 and H_2O. After this period, the conversion drastically decreased and reached a lower stable level (ca. 20%). As the activity decreased, methanol was formed along with CO_2. Phosphorus-containing products were not detected by GC. This feature was common for all the hydroxyapatite catalysts and the Pt/Al_2O_3 system as well, vide infra. No significant differences were observed between Ca-deficient hydroxyapatites and the stoichiometric one. However, substitution of 2.5% of the Ca by Cu increased the duration of the protection period by a factor of 2 and 20% substitution by a factor of 4. At this temperature, the conversion in a blank test (using glass beads) was 3%, independent of reaction time.

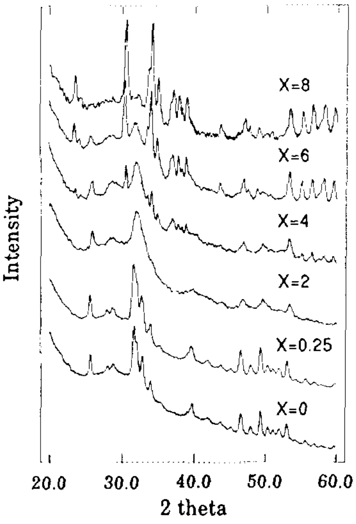


FIG. 2. X-ray diffraction patterns of Cu-substituted hydroxyapatite catalysts ($Cu_xCa_{10-x}(PO_4)_6(OH)_2$; x = 0, 0.25, 2, 4, 6, and 8 [Cu*X*-HA]).

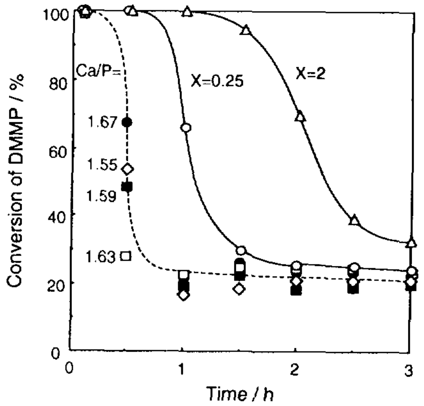


FIG. 3. Time courses of the conversion of DMMP over stoichiometric (●, Ca/P = 1.67), Ca-deficient hydroxyapatites (□, Ca/P = 1.63; ■, Ca/P = 1.59; ◇, Ca/P = 1.55), Cu0.25-HA (○), and Cu2-HA (△) [temperature, 573 K; DMMP concentration, 2.885×10^{-5} mol/l; total flow rate, 100 ml/min; O_2/N_2 = 1/4; catalyst weight, 0.3 g].

Since a positive effect was observed by substitution of Cu, the effect of Cu concentration was investigated. Even though all the Cu-modified hydroxyapatite catalysts (Cu*X*-HA; *X* = 0.25, 1, 2, 4, and 8) showed a similar variation with time, their effectiveness varied. This is illustrated in Fig. 4a, where their protection periods at 573 K are compared. (The BET surface areas are shown in parentheses.) A volcano-like pattern was obtained; Cu2-HA was the most active for the oxidative decomposition of DMMP and the protection period against DMMP was about 1.3 h, twice as long as that of Cu0.25-HA. The protection period of Cu2-HA could be extended to ca. 3 h by use of twice the amount of the catalyst, suggesting that it was being poisoned by the PO_x deposited during the oxidative decomposition. In order to elucidate the effect of the increase of the total surface area on the activity of Cu-substituted hydroxyapatite catalysts, the dependence of the activity on the Cu content was replotted in Fig. 4b after a normalization to the BET surface area. Cu2-HA was still the best catalyst; although the magnitude of the changes decreased, the trend of the volcano-like shape was maintained. This shows that the variation of the catalytic activity cannot be entirely attributed to the changes in the surface area.

The temperature dependency of the oxidative decomposition of DMMP over Cu2-HA was examined and the results are presented in Fig. 5. At 373 K, 100% conversion of DMMP was observed for only 5 min; however, no products were obtained. At 473 K, the formation of CO_2

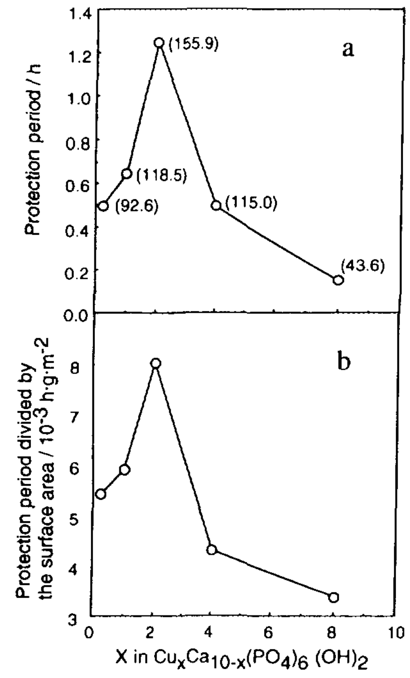


FIG. 4. (a) Dependence of the protection period on the substituted amount of Cu at 573 K. The numbers in parentheses refer to the BET surface areas. (b) After normalization to the surface area of the Cu-substituted hydroxyapatites.

and H_2O in the 100% region was observed. Both the activity and the protection period were markedly enhanced by raising the temperature to 673 and 773 K. At these temperatures, 100% conversion could be maintained for over 7.5 and 9 h, respectively, and about 70% conversion could be kept for over 30 h at 673 K. In other words, this catalyst could be of practical interest at these higher temperatures.

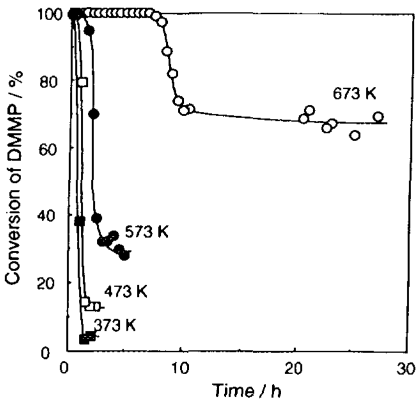


FIG. 5. Temperature dependence of the oxidative decomposition over $Cu_2Ca_8(PO_4)_6(OH)_2$. ■, 373 K; □, 473 K; ●, 573 K; ○, 673 K [DMMP concentration, 2.885 × 10^{-5} mol/l; total flow rate, 100 ml/min; O_2/N_2 = 1/4; catalyst weight, 0.3 g].

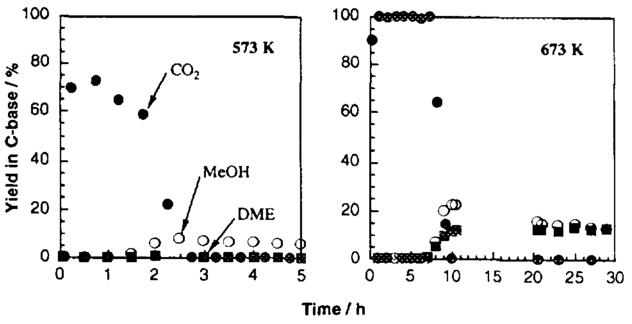


FIG. 6. Product distribution for the oxidative decomposition of DMMP over Cu2-HA at 573 and 673 K. Yield (%) = (number of C atoms in each product)/(number of C atoms in the DMMP introduced) × 100.

The product distributions of the oxidative decomposition of DMMP over Cu2-HA at 573 and 673 K are shown in Fig. 6. During the protection period, only CO_2 and H_2O were formed. The CO_2 yield was 100% at 673 K but only 70% at 573 K where presumably some partially decomposed products remained on the surface. CO_2 formation decreased as the catalyst deactivated. This was accompanied by the appearance of methanol (and dimethyl ether at 673 K).

Regeneration of Cu-Substituted Catalyst

For the practical purpose of defense equipment, a high-performance catalyst that will operate at low temperature is thought necessary (9). At 573 K, even though all the Cu-modified hydroxyapatite catalysts had an acceptable initial activity, they became deactivated after a short period of time. A series of experiments was carried out to investigate the causes of deactivation and the possibility of regeneration. Cu0.25-HA catalyst was selected for this purpose; it was severely deactivated after 2 h at 573 K as shown in Fig. 3. It was chosen because XRD indicated that it was better crystallized (showed a more perfect apatite structure than Cu2-HA). The deactivated catalyst was treated in flowing O_2 for 1 h at 573 K or at 773 K, respectively, and the reactions were repeated at 573 K. The results are shown in Fig. 7. While only a small fraction of the initial activity was recovered after 573-K regeneration, after 773 K the initial activity was fully regenerated. On the other hand, Cu2-HA which showed the highest activity was only partially regenerated by the 773-K oxidation after reaction at 573 K for 3 h (the protection period after regeneration was less than 30 min). These data suggest that the catalyst is deactivated by phosphate residues which can migrate from the active site to the support at high temperature, but not at 573 K. A limited capacity of the support for storage of phosphate residues may be the explanation of the partial regeneration of Cu2-HA.

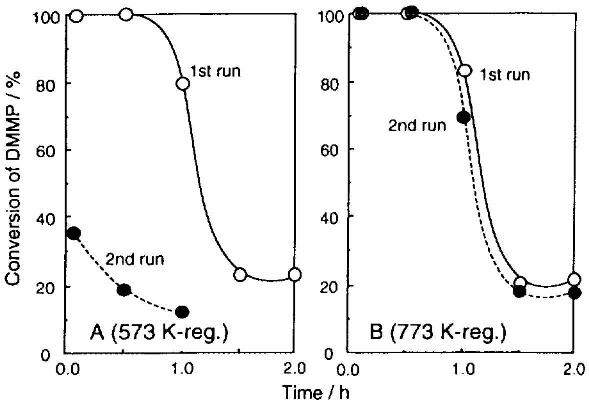


FIG. 7. Regeneration of the deactivated Cu0.25-HA catalyst. (A) First run at 573 K (○); 2nd run at this temperature after oxidation at 573 K for 1 h (●). (B) First run at 573 K (○); 2nd run at this temperature after oxidation at 773 K for 1 h (●). Reaction conditions were the same as those in Fig. 3.

Study of Catalyst Deactivation and Regeneration

The changes which occurred during use and regeneration were investigated using several analytical methods. Some results for Cu0.25-HA are summarized in Table 1. XRD data showed no significant changes of the bulk structure occurred during reaction at 573 K. XPS binding energy measurements also showed that the P2*p* *binding energy* value was little affected by activation, reaction, or regeneration treatments. However, a significant change of the intensity of P2*p* peak was observed. The XPS area ratio [I(P2p)/I(Ca2p)] increased from 0.15 for the fresh catalyst (after 773-K pretreatment) to 0.25 after reaction at 573 K but was little changed (0.23) after regeneration at 773 K. These data suggest that phosphorus compounds formed during the oxidative decomposition of DMMP accumulated on the surface blocking the oxidation centers.

The state of the phosphorus compound was investigated by solid-state ^{31}P NMR. Before reaction, only one peak at 5.2 ppm was observed; this was due to phosphorus in the hydroxyapatite structure. There was no difference in the chemical shifts among Cu-modified hydroxyapatite catalysts. After reaction at 573 K, a new peak appeared at 27 ppm along with the peak at 5.2 ppm. According to the ^{31}P NMR chemical shifts summarized in Table 2, the former peak could be assigned to methylphosphonate (32). The peak at 27 ppm disappeared after oxidation treatment at 773 K. However, no peaks which could be attributed to phosphorus oxides (100–150 ppm) were detected following oxidation. This suggests that PO_x was transformed to a form of phosphate by reaction with H_2O formed during the reaction. If phosphoric acid were formed, its peak at 0 ppm would overlap that due to the hydroxyapatite (5.2 ppm). Note that somewhat lower values have been reported in the literature (Table 2).

TABLE 1

Changes of Cu0.25-HA by Reaction and Regeneration

	Activity[a] (% conversion)	XPS[b] I(P2p)/I(Ca2p)	^{31}P NRM[c] (ppm)
Fresh[d]	100	0.15	5.2
573-K reaction	ca. 20 (2 h)	0.25	27, 5.2
773-K regeneration	100	0.23	5.2

[a] Initial % conversion of DMMP at 273 K after each treatment; see Fig. 7.

[b] The ratio of peak areas

[c] The chemical shift referred to 85% phosphoric acid.

[d] The catalyst was pretreated for 1 h at 773 K in N_2.

TABLE 2

Chemical Shifts of ^{31}P NMR

Chemical shift (ppm)	Formula	Name	Reference
2.8	$Ca_{10}(PO_4)_6(OH)_2$	Calcium hydroxyapatite	(27)
2.3	$Ca_{10}(PO_4)_6(OH)_2$	Calcium hydroxyapatite	(31)
110	P_4O_6		(29)
150	P_4O_{10}		(30)
24	CH_3PO_3	Methylphosphonate	(32)
39.4	$(CH_3O)_2CH_3PO$	Dimethyl methylphosphonate	(28)

The change of the catalyst weight was followed by Cahn microbalance. The weight of the catalyst increased continuously with the time on stream at 573 K. The catalyst gained 14% over a period of 28 h. At this point the reactant gases were switched to oxygen and the temperature was increased by 1°/min in flowing O_2. The weight started to decrease at about 628 K. It reached another stable state at about 753 K. The weight loss during temperature programmed oxidation (up to 773 K) was only 14.6% of the weight gained during the 573-K reaction. The general conclusion is that the catalyst cannot be restored to its initial condition by this simple procedure.

IR Spectroscopy Study of the Transformation of Adsorbed DMMP by Heating

The transformation of adsorbed DMMP on Cu0.25-HA during heating in flowing O_2 was studied by IR using the *in situ* IR cell (Fig. 8). When the activated catalyst was exposed to the DMMP vapor at room temperature, four bands were observed (2993, 2960, 2927, and 2857 cm^{-1}) in the region of C–H stretching. The IR spectrum obtained after adsorption at room temperature was identical to that of liquid DMMP indicating that the DMMP was adsorbed in a molecular form on the Cu-substituted hydroxyapatite. According to Moravie *et al.* (33), the absorption bands at

2993 and 2927 cm^{-1} could be assigned to ν_{as}(C–H) and ν_s(C–H) of P–CH_3 group, respectively, while 2960 and 2857 cm^{-1} were due to the corresponding vibrations of the P–OCH_3 groups (Fig. 8). After 573-K oxidation, the intensity of the latter pair of bands (P–OCH_3) decreased much more relative to those at 2993 and 2927 cm^{-1} bands (P–CH_3). The P–OCH_3 bands disappeared after 673-K oxidation *versus* 773 K for the P–CH_3 peaks, showing that the methoxy groups are attacked preferentially. Interestingly, the compound is completely decomposed (or desorbed) after heating to 773 K, which means that the surface can be virtually completely cleaned of carbonaceous decomposition products at that temperature. This does not mean that PO_x compounds are not retained (Table 1).

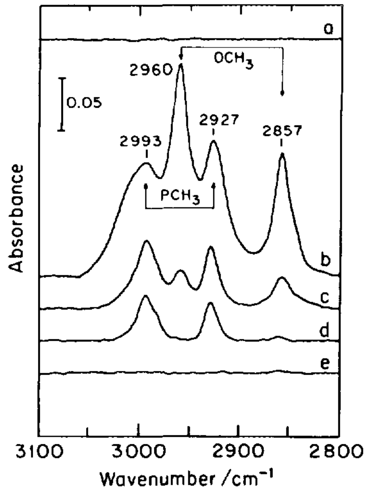


FIG. 8. IR spectra taken during decomposition of adsorbed DMMP on Cu0.25-HA by heating: (a) clean catalyst evacuated at 773 K for 1 h, (b) after DMMP adsorption for 1 h at room temperature and then evacuation for 30 min, (c) following a 573-K oxidation for 1 h, (d) after a similar oxidation for 1 h at 673 K, and (e) after a 773-K oxidation.

Comparison to Other Catalytic Systems

A comparison of the Cu2-HA catalyst with a sample of a Pt/TiO_2/cordierite catalyst (1.6 wt% Pt) was made. The latter was crushed and the 40–80 mesh fraction was used. When comparison was made on the basis of equal weights of catalyst, the behavior of the two catalysts was quite similar; both had protection periods of about 1.8 h. Since the catalyst was diluted by the cordierite, this comparison may not be fair. For a better comparison, several Pt-supported catalysts were prepared and their activities were examined (Fig. 9). All Pt-supported catalysts on γ-Al_2O_3, TiO_2, or hydroxyapatite (1.2 wt% Pt) showed higher activities than that of Cu2-HA. Among them, Pt/Al_2O_3 was the best catalyst and Pt/HA and Pt/TiO_2 showed similar behavior. The improvement was not so large, however, that compensation could not be made by increasing the weight and temperature of the Cu2-HA catalyst. As shown in Fig. 9, the protection period of Cu2-HA at 673 K (7.5 h) was comparable to that of Pt/HA and Pt/TiO_2 at 573 K (8 h). Doubling the weight of catalyst would make the result comparable with the Pt/Al_2O_3 catalyst. The product distributions were very similar among the Pt-supported catalysts as shown in Fig. 10. Only CO_2 and H_2O were formed during the protection period and the CO_2 yields were 100%. Methanol formation was concomitant with the deactivation of the catalysts.

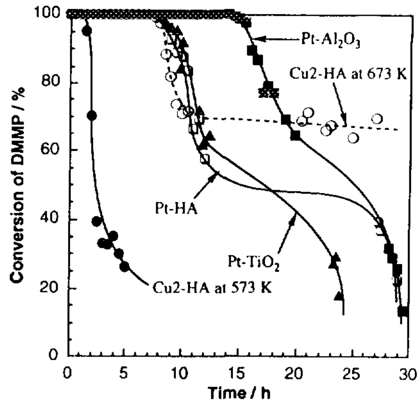


FIG. 9. Comparison of Cu2-HA with supported Pt catalysts: (●) Cu2-HA, (□) Pt/HA, (■) Pt/Al_2O_3, and (▲) Pt/TiO_2 all at 573 K, and (○) Cu2-HA at 673 K. Other reaction conditions are the same as those in Fig. 3.

The protection period of the 8 wt% Mo/γ-Al_2O_3 catalyst was 2.5 h, but unlike the Cu- or Pt-based catalysts, the principal product formed during the protection period was CO instead of CO_2.

DISCUSSION

Divalent cations such as Ba, Sr, Cd, and Pb have been substituted for Ca in hydroxyapatites. Some of these cations reportedly form solid solutions with Ca hydroxyapatite over the full range of composition. Cupric hydroxyapatite has been reported (24) to have a limited range of composition. Patel and Rao (34) reported the formation of a product that was identified as cupric hydroxyapatite but without any definite characterization. Misra (35) has reported that the interaction of an excess amount of aqueous cupric ions with calcium hydroxyapatite produced cupric orthophosphate, $Cu_3(PO_4)_2 \cdot 3H_2O$, and libethenite, $Cu_2(OH)PO_4$, instead of cupric hydroxyapatite. In the present work, solid solutions of Cu and Ca hydroxyapatite could not be obtained over the full range as shown in Fig. 2. A new species appeared at Cu4-HA assignable to $Cu_2(OH)PO_4$, which agrees well with Misra's report.

Hydroxyapatites have been used in prior work only as

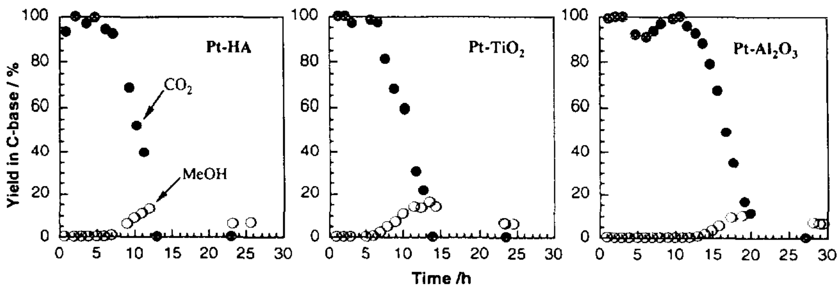
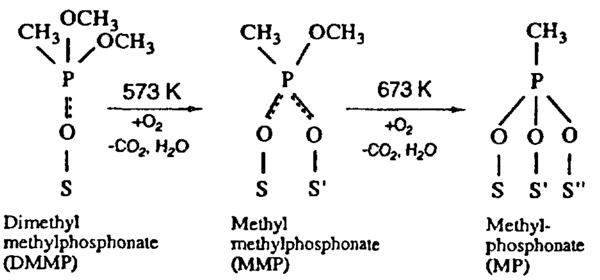


FIG. 10. Formation of CO_2 and CH_3OH in the oxidative decomposition of DMMP over Pt-supported catalysts at 573 K.

weak acid or base catalysts or for dehydrogenation of alcohols. However, it is well known that these materials have a cation exchange capacity. Hence, it was inferred that a redox property should be present in the Cu-substituted material. This was justified by the results presented in Figs. 3–6. To the best of our knowledge, this is the first study to use the hydroxyapatite as an oxidation catalyst.

On the basis of IR and NMR results, a mechanism for the reactions of DMMP on heating in O_2 could be proposed:



[2]

DMMP adsorbed at room temperature is partially decomposed to methyl methylphosphonate $[CH_3P(OCH_3)O_2]$ at 573 K, methyl phosphonate (CH_3PO_3) at 673 K, and finally totally decomposed at 773 K. Note that these data were collected for a good crystalline hydroxyapatite, Cu0.25-HA. Other preparations may be expected to scale somewhat differently with temperature. Cu2-HA produced 100% of CO_2 (within experimental error) at 673 K throughout the protection period (see Fig. 6).

Templeton and Weinberg (4, 5) showed, using inelastic electron-tunneling spectroscopy, that DMMP decomposed on Al_2O_3 into methyl methylphosphonate at 295 K and methyl phosphonate at 573 K, while the P–CH_3 bond was stable to at least 673 K. White and co-workers (2, 3) reported that on Pt(111), the PO–CH_3 bond was cleaved at 300–400 K; the P–CH_3 bond was cleaved at 400–500 K, leaving predominantly PO and an unidentified PO_x species which were stable to at least 500 K. Therefore, the decomposition mechanism of DMMP on Cu-hydroxyapatite may be quite similar to that on a Pt single crystal and on Al_2O_3.

In the present study, phosphorus containing gaseous products were not detected in the products from reaction at 573 K. The phosphorus concentration on the surface (determined by ESCA) was greatly enhanced during the reaction, but was not further changed (Table 1) even though the initial activity was recovered by the 773 K regeneration. Moreover, the weight gain of the catalyst during the reaction was not reversible by the 773 K oxidation. The following can be suggested from these results. A phosphorus residue is accumulated on the surface as a partially decomposed form of DMMP at 573 K, possibly methyl methylphosphonate, as was suggested by the IR results. The partially decomposed form of DMMP was totally transformed to PO_4^{3-} at 773 K. The regeneration of catalytic activity was due to the migration of phosphorus from the active site (Cu^{2+}/Cu^{+}) to the support (hydroxyapatite) which acted as a reservoir.

After deactivation, a sticky condensate was obtained at the exit of the reactor. This could be H_3PO_4, as Graven *et al.* (10) have reported for their Pt/Al_2O_3 system. The formation of H_3PO_4 can be explained by a hydrolysis of the partially decomposed form of DMMP by the H_2O produced by combustion.

Direct comparison among Cu2-HA (12 wt% Cu), Pt/Al_2O_3 (1.2 wt% Pt), and Mo/Al_2O_3 (8 wt% Mo) catalysts revealed that the order of activity per g-catalyst is Pt > Mo > Cu. Although Mo/Al_2O_3 was more active than Cu2-HA, it cannot be used as an alternative to Pt/Al_2O_3 since it produces CO instead of CO_2 during the protection period. As explained before, hydroxyapatite catalyst is cheap and readily available. The used catalyst may be discarded. Comparing the activities of Cu2-HA and Pt/Al_2O_3, as shown in Fig. 9, the Cu2-HA can match the Pt/Al_2O_3 if one uses twice the weight and 100° higher reaction temperature. This does not make it equally active; only that it may act as a reasonable substitute. In fact, at 673 K, the protection period achieved with 0.6 g of Cu2-HA was ca. 20 h. This temperature is too high for use in a simple single-pass reactor, but could find application in a more sophisticated system involving a well designed heat exchanger. Therefore, it may be concluded that Cu2-HA can be an effective catalyst for nerve gas decomposition and may be substituted for the conventional catalytic system based on the noble metal.

CONCLUSION

1. For the oxidative decomposition of DMMP, hydroxyapatite catalysts showed 100% conversion at the beginning of the reaction at 573 K but quickly lost this ability after a time defined as the "protection period." During this period, the products were CO_2 and H_2O, while CH_3OH was formed during deactivation.

2. The catalytic activity of hydroxyapatite was markedly increased by substitution of Cu for Ca. Among Cu-substituted hydroxyapatites, Cu2-HA incorporated the most Cu while maintaining the apatite structure and showed the highest activity.

3. Adsorption and partial decomposition of DMMP occurred at 373 and 473–573 K, respectively.

4. Total decomposition of DMMP occurred at 673–773 K. Phosphorus compounds which were produced during the decomposition could not be eliminated from the surface even after 773-K oxidation. The regeneration of catalytic activity appears to be due to the migration of these materials to the support which acts as a reservoir.

5. $Cu_2Ca_8(PO_4)_6(OH)_2$ catalyst, which can be prepared easily and cheaply, exhibits high catalytic activity for DMMP decomposition and could constitute a practical catalytic defense system against nerve gases in warfare.

ACKNOWLEDGMENTS

This work was supported by funds made available by the Materials Research Laboratory of the University of Pittsburgh. The authors are grateful to Dr. Chen C. Hsu for a sample of Pt/TiO_2/cordierite and for helpful discussions. Thanks are due also to Professor N. Eror and Mr. T. MacNamara for preparation of Ca-deficient and Pt-coated hydroxyapatites, and for measurements of surface areas.

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