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Catalytic Oxidation of Dimethyl Methylphosphonate

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The catalytic oxidation in air of dimethyl methylphosphonate (DMMP), a nerve gas stimulant, has been studied over laboratory-prepared Pt/Al_2O_3 as a function of Pt loading (0.5 or 2.0%) and temperature (150, 250, or 400°C). At 250°C and residence time of 0.69 s, carbon balances indicate that 90–95% of the C atoms in the DMMP feed were completely oxidized to CO_2 during the periods when DMMP destruction was >99% (50 h for the 0.5% Pt catalyst and 76 h for the 2.0% Pt catalyst). Only after the end of these protection periods was methanol detected in the gaseous effluent. HPLC analysis of a product liquid showed that four intermediate P-containing compounds were formed: dimethyl phosphate (DMP), monomethyl phosphate (MMP), monomethyl methylphosphonate (MMMP), and methylphosphonic acid (MPA). A reaction scheme is proposed to account for the production of these intermediates by a series of oxidative and hydrolytic reactions. Different behavior was observed at 400°C. Although the period of complete DMMP destruction was very long (>135 h) with 0.5% Pt catalyst, oxidation as measured by CO_2 production was incomplete and the oxidation activity decreased with time on stream. At 400°C the hydrolytic reactions apparently become sufficiently efficient to effect complete DMMP conversion for extended periods despite the drop in oxidation activity. Several methods of characterizing deactivated catalyst provide incremental evidence that catalyst alumina reacts with product phosphoric acid to give $AlPO_4$. © 1994 Academic Press, Inc.

INTRODUCTION

The standard method of removing toxic war gases has been sorption by activated charcoal, sometimes impregnated with Cu and Ag salts. Development of potent anticholinsterase nerve gases compounded the problem of protection since the nerve gases cannot be tolerated even in small amount. A decrease from 100 to 99% removal constitutes "breakthrough."

An alternative method for protection against nerve gases is catalytic oxidation, studied by one of the authors 30 years ago (1, 2). At that time a scoping survey of catalysts commercially available led to the study of Pt/Al_2O_3 as the most promising candidate for this application.

Laboratory testing of nerve gases is hazardous. Use of dimethyl methylphosphonate (DMMP) as a relatively nontoxic stimulant was introduced in the research of Graven *et al.* (1). DMMP is a liquid having a vapor pressure at 298 K of 1.05 Torr (1 Torr = 133.3 Nm^{-2}). Its chemical structure resembles somewhat that of the toxic agent isopropyl methyl fluorophosphonate (GB); both are derivatives of methylphosphonic acid. Results on the catalytic conversion of GB were reported by Baier and Weller (2). In their results at 400°C, complete oxidation of GB occurred for only a few hours; however, as the oxidation activity decreased, dealkylation of the isopropyl side chain occurred by an acid-catalyzed mechanism. Side chain dealkylation to an olefin cannot occur with DMMP. Baier and Weller also determined that only half of the large catalyst weight gain, 44%, after a long run could be removed by Soxhlet extraction with water for a week. Accumulation of, and deactivation by, aluminum phosphate in the catalyst was suggested.

Neither Graven *et al.* nor Baier and Weller carried out a carbon balance during the reaction, and phosphorous-containing intermediates were not identified.

Hegedus and Gumbleton (3) and Kirchner and co-workers (4–6) studied the poisoning of Pt oxidation catalysts by phosphorus, mainly in the context of auto exhaust catalysts. This research does not bear directly on the problem of complete removal of nerve gases at relatively low temperatures. Hsu and Pistritto studied DMMP oxidation over a Degussa three-day catalyst (7). They found that at 400°C, 96% of the inlet DMMP was removed for an on-stream time of 18 h. In their work neither carbon balance nor possible intermediate organophosphorus compounds were investigated.

The present work had several objectives:

(a) To study the fate of carbon atoms during the catalytic oxidation of DMMP by establishing carbon balances during the period of complete DMMP removal.

(b) To identify intermediate phosphorus-containing compounds in the reactor effluent after DMMP breakthrough, and to suggest a reaction scheme consistent with the observed intermediates.

(c) To look for evidence bearing on the production of aluminum phosphate in the catalyst by reaction of catalyst alumina with product phosphoric acid.

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EXPERIMENTAL

Catalyst

Two catalysts were prepared, one containing 2.14% Pt, the other 0.50% Pt. These will be referred to hereafter as 2 and 0.5% Pt. Both were prepared by impregnation of a Davison alumina, Lot No. 10867-18, with aqueous chloroplatinic acid solution, followed by drying at 110°C and air calcination at 500°C. The support was a γ-alumina of surface area 234 m^2/g (BET) or 294 m^2/g(Hg), with average pore diameter 126 Å. The alumina was ground and sieved to 20–40 mesh (0.85–0.43 mm) before impregnation. Some tests were also made with a commercial reforming catalyst, Boudry 3H.

Equipment

A conventional flow system was used for the activity studies. A metered flow of high purity air was passed through a saturator containing liquid DMMP at room temperature. Concentration of DMMP in this feed stream was determined in each run by sampling the stream with a gas-tight syringe through a sampling port just before the reactor. A similar port was placed immediately after the reactor. The sample from the effluent port permitted GC/FID analysis of DMMP, methanol, and methyl ether in the product stream. A small glass trap was placed inline, close to the reactor end but after the sampling port. Unreacted DMMP, product phosphoric acid, and intermediate P-containing products in the effluent stream collected in this trap. Analysis of product CO_2 and H_2O was made with a separate in-line GC/TCD. The catalyst was supported on glass wool in a glass reactor of 6.6 mm I.D.

Activity Testing

The catalyst charge was typically 1.5 g (3.8 cm^3). The catalyst was brought to 300°C at 10°C/min in flowing He and reduced *in situ* in flowing H_2 for 1 h at 300°C, followed by a purge in flowing He for 1 h. After the He purge and adjustment of temperature to the desired reaction temperature (400, 250, or 150°C), pure air was allowed to flow through the reactor for 5 min. DMMP was then introduced into the air stream through the saturator. The flow rate of air (measured at room temperature) was kept constant at 175 cm^3/min. This corresponded to residence times (at reaction temperature) of 0.80 s at 150°C, 0.69 s at 250°C, and 0.54 s at 400°C. Feed rate of DMMP was approximately 0.074 g/h.

Characterization of Deactivated Catalyst

A sample of Houdry reforming catalyst was examined after a 32-h on-stream period with DMMP. After measurement of weight gain, the sample was extracted with water in a Soxhlet apparatus for 24 h and the extract was studied by various methods, including determination of total P content. The extracted and dried catalyst was in turn studied by several methods: SEM–EDAX, IR, and total water-insoluble phosphorus. The SEM–EDAX studies gave no useful results and will not be further discussed. IR absorption was determined on ground samples mulled in mineral oil. Comparisons of IR spectra were made with literature data and with samples of γ-alumina and aluminum phosphate. Determination of total P in the extracted sample, presumed to be present as water-insoluble aluminum phosphate, was made by standard wet chemical analysis—dissolution in hot, dilute HCl followed by colorimetric determination of phosphate.

Identification of Liquid Products

Water-soluble liquid products from DMMP oxidation were observed in three circumstances: (a) by Soxhlet extraction with water of deactivated catalyst, (b) in liquid condensate in the in-line glass trap during a run with the Houdry catalyst which had short protection time, and (c) by water washing of a light fog that appeared at the exit end of the reactor during oxidation with the long-lived catalysts described in this paper. The results of acid–base titration, IR, and colorimetric analyses before and after persulfate oxidation of organophosphates have been previously described (8, 9)

HPLC analysis was used for identification of phosphorus-containing compounds in the liquid condensate from a run with reforming catalyst, and in water washings of the fog deposited during the long runs described below. The HPLC analysis was made with a Waters HPLC and Interaction Ion 300 column. Standard aqueous solutions of DMMP and possible reaction products—phosphoric acid (PA), methylphosphonic acid (MPA), monomethyl phosphate (MMP), and dimethyl phosphate (DMP)—were used for determination of retention times.

RESULTS AND DISCUSSION

Reaction Kinetics and Product Identification

A number of runs of long duration were made. Four of these with laboratory-prepared catalysts, chosen to illustrate the effects of Pt loading and temperature, are described in Table 1. Experimental results corresponding to these runs are summarized in Figs. 1 and 2.

Comparison of the behavior of 2% Pt catalyst (Run 1) with that of 0.5% Pt catalyst (Run 3) at 250°C is shown in Fig. 1. (A duplicate of Run 1, carried out with a fresh catalyst sample, gave results almost identical with those of Run 1; these are not shown in the figure). Figure 1A displays (a) the CO_2 yield, as a percent of the stoichiometric value which would result if every carbon atom in

TABLE 1

Conditions for Activity Tests[a]

Run No.	Pt in Catalyst (%)	Temperature (°C)	Run duration (h)
1	2	250	80
2	2	150	8
3	0.5	250	62
4	0.5	400	135

[a] Residence time is 0.69 s at 250°C and 0.54 s at 400°C. Air flow rate at room temperature is held constant.

DMMP were oxidized to CO_2, as a function of time on stream (TOS), and (b) the H_2O yield, in arbitrary units. Figure 1B is a plot of unconverted DMMP appearing in the effluent, as a percent of the inlet concentration, vs TOS. Solid curves pertain to Run 1, dashed curves to Run 3. These results at 250°C show that:

(a) The production of CO_2 is almost stoichiometric during the entire period before breakthrough; it is about 95% of theoretical for the 2% catalyst and about 90% for the 0.5% catalyst.

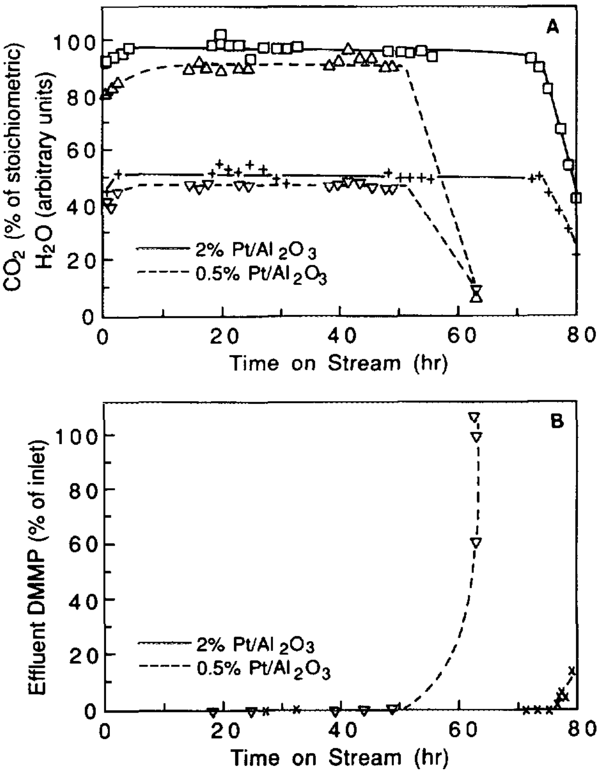


FIG. 1. (A) Effect of Pt loading (0.5% Pt vs 2.0% Pt) at 250°C on production of carbon dioxide and water, as a function of time on stream. (B) DMMP concentration in reactor effluent (relative to inlet concentration) as a function of time on stream at 250°C. Solid curves pertain to 2.0% Pt in catalyst, dashed curves to 0.5% Pt.

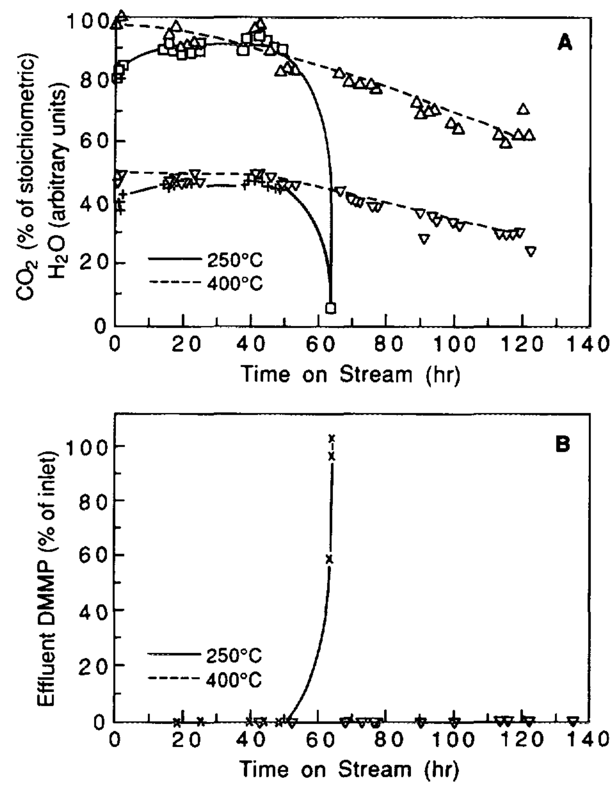


FIG. 2. (A) Production of carbon dioxide and water with 0.5% Pt catalyst at 400°C or 250°C, as a function of time on stream. Dashed curves pertain to 400°C, solid curves to 250°C. (B) DMMP concentration in reactor effluent (relative to inlet concentration) as a function of time on stream at 400° or 250°C.

(b) Not surprisingly, the 2% catalyst affords a longer protection time than does the 0.5% catalyst (75 vs 50 h).

An experiment at 150°C (Run 2 in Table 1) resulted in a protection time of only 5–6 h. Furthermore, the CO_2 production never exceeded 50% of theoretical at 150°C, and even this value was observed only for a period of about 2 h on stream.

Run 4 (in Table 1) was conducted at 400°C. Since the protection time was already very long (76 h) at 250°C with 2% Pt catalyst, only the 0.5% Pt catalyst was tested at 400°C. Figure 2 shows a comparison of results with the 0.5% Pt catalyst at 400°C with those at 250°C.

Run 4 was arbitrarily terminated at 135 h on stream, at which time there was still no detectable DMMP in the reactor effluent. The curve for effluent DMMP in Run 4 is simply superimposed on the base line in Figure 2B; i.e., the protection time exceeded 135 h. By contrast, the trends for CO_2 and H_2O production at 400°C were qualitatively different from those at 250°C. The yields of both of these gaseous products declined during the course of the run, even though no DMMP was appearing in the effluent. Clearly a reaction route other than complete oxidation played a role at the higher temperature.

After breakthrough occurs and oxidation activity declines, one may expect to see reaction products other than aluminum phosphate, CO_2, and H_2O. This applies both to gaseous products and to organophosphorus intermediates. Methanol can be formed by hydrolysis of the methoxy groups in DMMP. Although product methanol should be oxidized as long as high oxidation activity exists, methanol could survive and be seen in the exit stream after breakthrough occurs. This was observed.

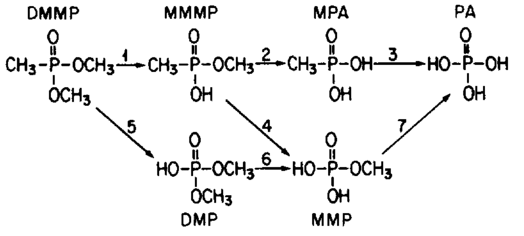
A peak for methanol started to be seen in the GC analyses at the beginning of DMMP breakthrough. To be specific: in Runs 1, 3, and 4 the protection times were about 75, 50, and >135 h, respectively. In Runs 1 and 3 methanol was first seen in the effluent at about 70 and 50 h, respectively. In Run 4 neither DMMP nor methanol appeared for the on-stream period of 135 h.

The search for phosphorus-containing intermediates was conducted by HPLC analysis of two liquid samples. One sample was the trap condensate (diluted with water) from a separate experiment which had been deliberately continued after breakthrough. The second sample was the water washings of the light fog observed at the end of Run 1.

Figure 3 shows the HPLC chromatogram of the trap condensate. Six peaks for P-containing compounds were observed. In the order of increasing residence time, the peaks corresponded to dimethyl phosphate (DMP), monomethyl phosphate (MMP), phosphoric acid (H_3PO_4), (attributed to) monomethyl methylphosphonate (MMMP), methylphosphonic acid (MPA), and DMMP.

The chromatogram for the water washing of the fog at the end of Run 1 showed only 3 peaks. The first was identified as DMP; the second was attributed to MMMP; the third peak corresponded to DMMP.

We suggest the following reaction scheme to explain the origin of these species:



In this scheme DMMP first reacts to give either MMMP (step 1) or DMP (step 5). MMMP then reacts stepwise either to (a) MPA (step 2) and to phosphoric acid (step 3), or (b) by an alternate route to MMP (step 4) and to phosphoric acid (step 7). The conversion of DMP to phosphoric acid occurs through steps 6 and 7.

Steps 1 and 2 are successive replacements of the two methoxy groups in DMMP by hydroxyl groups. These steps may occur either by oxidation or hydrolysis under reaction conditions. Methanol, the other product of hydrolysis, may (or may not) be further oxidized to HCHO or finally to CO_2 and H_2O. Breaking the C–P bond in steps 3, 4, and 5 is presumed to require reaction with oxygen. The DMP and MMMP observed in the liquid chromatograms are initial reaction products arising from steps 1 and 5, respectively, in the reaction scheme. Steps 1, 2, 6, and 7 may all involve only hydrolysis.

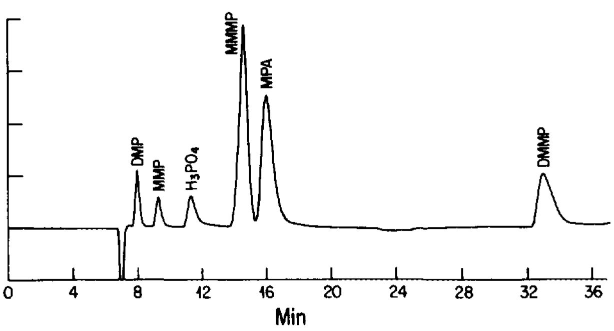


FIG. 3. HPLC chromatogram of liquid product. Peaks for phosphorus-containing species are labeled (see text).

The nature of the phosphorus compound retained in the catalyst should also be addressed. Baier and Weller (2) had suggested that alumina reacts with product phosphoric acid to give noncrystalline aluminum phosphate which clogs catalyst pores. The studies of Hegedus and Gumbleton (3) and by Kirchner *et al.* (4–6) are largely concerned with the kinetics and modeling of P poisoning in exhaust catalysts, rather than with analysis of reaction products. The present paper provides some additional information:

(a) The IR spectrum of badly deactivated catalyst (as a mull in mineral oil) resembled that of fresh catalyst, with a major exception: there was a very strong and broad peak centered at about 1100 cm^{-1}. This peak is absent in the spectrum of alumina, but it is a dominating feature in the spectrum of $AlPO_4$.

(b) Actual weight gain of the used catalyst after being run with DMMP, and after water extraction and drying, was 27%. Wet chemical analysis of total phosphate in this sample corresponded to a calculated weight gain of 23%. The small difference may result from residual water after water extraction and drying.

(c) Total phosphorus in the water extract of the used catalyst, determined by colorimetry after persulfate oxidation of all organophosphates, was only 7% of the amount remaining in the catalyst after extraction for 24 h. $AlPO_4$ has very low solubility in water.

(d) A Houdry reforming catalyst, having an initial area of 193 m^2/g, showed a short protection period against DMMP even at 400°C. After 32 h on stream at 400°C, the area had decreased to 51 m^2/g. Soxhlet extraction of the deactivated catalyst with water and subsequent drying at 300°C resulted in a recovery in area only to 71 m^2/g.

These results on used catalyst are consistent with the conclusion that most of the P-containing product retained by the catalyst at the end of the onstream period is $AlPO_4$.

CONCLUSIONS

(a) Long periods of complete removal of DMMP can be achieved with a laboratory-prepared Pt/Al_2O_3 catalyst at 250°C. This period was 50 h with catalyst containing 0.5% Pt and 76 h with catalyst containing 2% Pt.

(b) During the period of complete DMMP removal at 250°C, the production of CO_2 from DMMP was 90–95% of theoretical.

(c) At 400°C, the protection time was more than 135 h; however, the CO_2 production declined steadily over the course of this period.

(d) Methanol from the hydrolysis of methoxy groups in DMMP appeared in the reactor effluent only after DMMP breakthrough.

(e) Liquid product collected after DMMP breakthrough showed the presence of four intermediate P-containing compounds: dimethyl phosphate, monomethyl phosphate, monomethyl methylphosphonate, and methylphosphonic acid. A reaction scheme involving a mix of oxidative and hydrolytic reactions is proposed to account for the production of these compounds.

(f) Measurements on a deactivated catalyst provided evidence that the P compound present in used catalyst is $AlPO_4$. The IR spectrum of used catalyst showed a peak around 1100 cm^{-1} that is characteristic of $AlPO_4$ but is not present in the spectrum of Al_2O_3. The measured weight gain of the catalyst, after water extraction and drying, agreed well with the weight gain calculated from wet chemical analysis for total P in the catalyst, on the assumption that the P was present as $AlPO_4$. Only a fraction (7%) of the P present in the used catalyst could be removed by Soxhlet extraction with water for 24 h.

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