Partial oxidation of ethane on silica-supported 12-molybdophosphoric acid in the presence of tetrachloromethane

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Received 22 May 1995; accepted 29 March 1996

The introduction of small quantities of tetrachloromethane (TCM) into the feedstream in the oxidation of ethane with nitrous oxide on 12-molybdophosphoric acid (HPMo) supported on silica increases the conversion but has little effect on the selectivities. In the presence of TCM the primary products appear to be ethylene, acetaldehyde and ethyl chloride. Studies of the effects of loading, time-on-stream, contact time and reaction temperature provide evidence for the importance of a loading corresponding approximately to a monolayer of HPMo, the HPMo anion in the production of acetaldehyde and TCM in both the production of ethyl radicals and the selectivity to acetaldehyde.

Keywords: ethane; partial oxidation; 12-molybdophosphoric acid; tetrachloromethane

1. Introduction

The oxidation of alkanes has been, and continues to be, the focus of intensive research effort (see, for example, ref. [1]). While in recent years methane has received considerable attention as a consequence of its predominance in natural gas, less work has been reported on ethane [1–37]. However, the oxidation of ethane is of both applied and fundamental importance, since products such as ethylene and acetaldehyde are precursors to consumer products and for reasons of increasing our knowledge of oxidation processes in general and of methane conversion in particular.

Earlier work from this laboratory has shown that metal–oxygen cluster compounds (MOCC) (also known as heteropoly oxometalates), in particular 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$, abbreviated to HPMo) supported on silica gel, catalyze the partial oxidation of methane to formaldehyde and methanol [38–40] and further, that silica itself possesses catalytic properties for this process [41]. Further, the supported catalyst appears to have a higher thermal stability than the unsupported solid [42–45]. Studies subsequent to the above have introduced small quantities of carbon tetrachloride (TCM) into the methane conversion feedstream with 12-molybdophosphoric acid, 12-tungstophosphoric acid (HPW) [46–48] and a wide variety of other inorganic solids [49]. With the latter solids both the conversion of methane and the selectivity to C_2 compounds was increased as a result of the addition of TCM, while with HPW, for example, selectivities to methyl chloride as high as 80% were observed [48].

In the present work the effect of the introduction of TCM to the ethane feedstream with $HPMo/SiO_2$ is studied, for various loadings of the catalyst on the support, reaction temperatures, contact times and times-on-stream.

2. Experimental

2.1. Materials

The supported MOCC were prepared by the impregnation of silica (Grace-Davison 400, 80–20 mesh) with aqueous solutions of HPMo (BDH Analar), which had been recrystallized from aqueous solution by a variation on the etherate method [50]. Ten grams of support were impregnated with 20 ml of aqueous acidic solution, followed by evaporation to dryness at 80°C and heating at 350°C for 2 h. All gases, He (Linde 99.9%), C_2H_6 (Linde CP Grade), O_2 (CP Grade) and N_2O (Matheson 99.0%) were used without further purification.

2.2. Reactions

A fixed-bed continuous flow reaction system equipped with appropriate valves and flowmeters was employed for the present work. The reactor, constructed from quartz tubing, 22.2 cm long and 0.9 cm o.d., was held horizontally in a temperature-controlled tubular furnace. The temperature was monitored by a thermocouple located at the catalyst bed. The reaction system was constructed from 1/8 inch o.d. stainless steel tubing heated, where appropriate, to prevent condensation. A

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six-port gas sampling valve (VALCO) with a 1.5 ml sampling loop was connected to the reactor exit and to a reactor by-pass to facilitate analyses of both reactor inlet and outlet streams. The catalyst was preheated in situ in a helium flow (30 ml min^{-1}) for 1 h at the reaction temperature, unless indicated otherwise. Where desired, tetrachloromethane was introduced to the system by flowing a separate stream of helium through a gas dispersion tube in a glass saturator containing the liquid at ice–water temperature. The flow of helium was adjusted so that after dilution following introduction into the main reactant stream appropriate concentrations of the additive were obtained.

The reactants and products were analyzed with an onstream Hewlett-Packard 5890 gas chromatograph equipped with a thermal conductivity detector. A Heysep Dip (HD) column (15 ft, programmed 40–200°C) was used to analyze for C_2H_6, N_2O, CH_4, C_2H_4, C_2H_5Cl, CO_2 and CH_3CHO). A 5A molecular sieve (MS) column (20 cm, 40°C) was employed for the analysis of O_2, N_2 and CO. Both columns were connected in series through a by-pass switching valve to isolate the MS column while CO_2, H_2O and hydrocarbons eluted from the HD column. The calibrations were made for each component under simulated analysis conditions. The carbon mass balances were 100(±5)%.

The reaction was followed from the initial to steady state with periodic analyses. The conversion of ethane was calculated on a carbon account – for basis. The selectivities were calculated as mole percentages of the products CO, CO_2, C_2H_4, CH_3CHO and C_2H_5Cl. A small quantity of CH_4 was produced but not recorded.

3. Results

The introduction of small quantities of TCM into the ethane/N_2O feedstream with 20 wt% HPMo/SiO_2 at 450°C substantially increases the conversion of ethane from very small values up to approximately 4% (fig. 1). The addition of larger amounts of TCM has relatively little additional effect. In contrast, the selectivities remain relatively unchanged at approximately 45 and 35% for acetaldehyde and ethylene, respectively, although a slight decrease is observed with the latter product. The selectivities to CO and to CO_2 decrease and increase, respectively, but to a relatively small extent, with increase in the quantity of TCM and become constant for quantities of TCM greater than about 0.2 mol%. With increasing quantities of TCM, the selectivity to C_2H_5Cl follows a nearly identical path as that of CO_2, first increasing and then becoming almost constant for quantities of TCM greater than 0.2 mol%.

In the absence of TCM and at a reaction temperature of 540°C the conversion passes through a maximum with increasing loading of HPMo on the support at approximately 20 wt% HPMo/SiO_2 (fig. 2A). Concomitantly the selectivity to acetaldehyde decreases continuously while that to ethylene increases. The selectivities to CO and CO_2 increase to a lesser extent as the loading is increased up to 40%.

In the presence of 0.2 mol% TCM in the feed a maximum in the conversion is again observed at approximately 20 wt% HPMo/SiO_2 (fig. 2B) and a reaction temperature of 450°C. The selectivities to acetaldehyde and ethylene decrease and increase, respectively, with

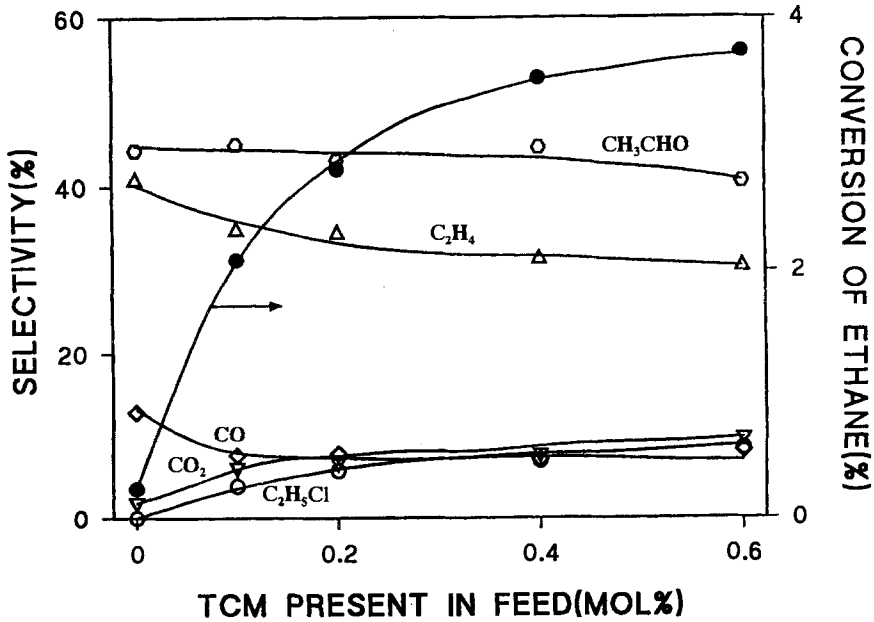

Fig. 1. Effect of amount of TCM in the feed on conversion and selectivity over 20 wt% HPMo/SiO_2: T_R = 450°C, W = 0.5 g, F = 25 ml/min, C_2H_6/N_2O = 4/1. (●) Conversion of C_2H_6, (◇) selectivity of CO, (▽) CO_2, (△) C_2H_4, (○) CH_3CHO, (○) C_2H_5Cl.

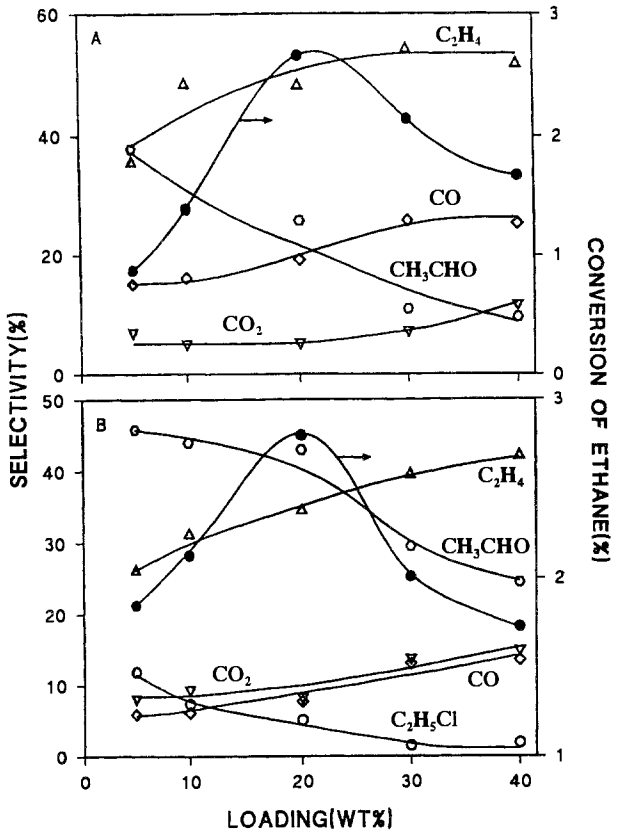

Fig. 2. Effect of loading of the HPMo on ethane conversion and selectivity over supported catalysts in the presence and absence of TCM: $W = 0.5$ g, $F = 25$ ml/min, $C_2H_6/N_2O = 4/1$. (A) $T_R = 540°C$, TCM absent, (B) $T_R = 450°C$, TCM present (0.2 mol% in the feed). Same symbols as in fig. 1.

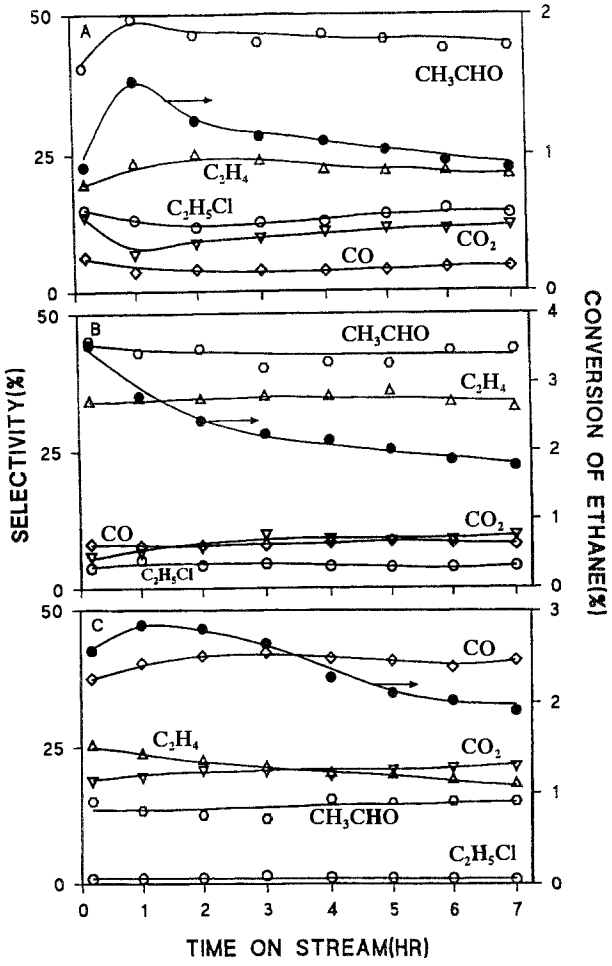

Fig. 3. Effect of time on stream on ethane conversion and selectivity over 20 wt% HPMo/SiO_2 in the presence of TCM: $W = 0.5$ g, $F = 25$ ml/mn, TCM = 0.2 mol% in feed, C_2H_6/oxidant = 4/1. (A) $T_R = 375°C$, N_2O as oxidant, (B) $T_R = 450°C$, N_2O as oxidant, (C) $T_R = 450°C$, O_2 as oxidant. Same symbols as in fig. 1.

increase in loading. Although the changes are less severe than those observed with acetaldehyde and ethylene the selectivities to CO and CO_2 increase almost in parallel while that to ethyl chloride decreases with loading.

With increasing time on stream (TOS) up to 7 h the selectivities to all products change relatively little with either N_2O or O_2 as oxidant and regardless of the temperature (fig. 3). However, in all cases the conversion decreases with TOS although the change is less severe at the lower temperature of 375°C. The use of oxygen in place of N_2O reduces the selectivity to acetaldehyde by at least a factor of three while increasing that to CO.

Increasing contact time produces the expected increase in conversion in either the absence or presence of TCM (fig. 4). In the absence of TCM both the selectivities to acetaldehyde and ethylene decrease with increasing contact time, but with TCM present the selectivity to ethylene remains essentially constant. The selectivity to ethyl chloride decreases with contact time.

The conversion of ethane increases continuously with increase in reaction temperature up to 500°C. In contrast, the selectivity to acetaldehyde changes relatively little up to a reaction temperature of approximately 450°C but for higher temperatures decreases significantly, while that to ethylene increases (fig. 5).

The rates of conversion of ethane and the selectivities to the products are shown for various partial pressures of ethane and nitrous oxide in fig. 6. These experiments were performed at constant reaction temperature and space velocity. The partial pressures of ethane or nitrous oxide were varied while the partial pressures of the remaining reactants were held at constant values. The flow of helium was adjusted to obtain the required space velocity. The overall rate of ethane conversion may be described by

$$\frac{-d[C_2H_6]}{dt} = k[C_2H_6]^{0.7}[N_2O]^{0.6}$$

for $P_{C_2H_6} = 0.1$–0.8 atm and $P_{N_2O} = 0.1$–0.6 atm. As is evident from fig. 6, low values of the molar ratio N_2O/C_2H_6 favour the production of ethylene and acetaldehyde, while the selectivities to CO and CO_2 show the opposite trends.

For one set of experimental conditions, the reaction of the products of the partial oxidation of ethane, namely, ethylene and ethyl chloride, in the absence and

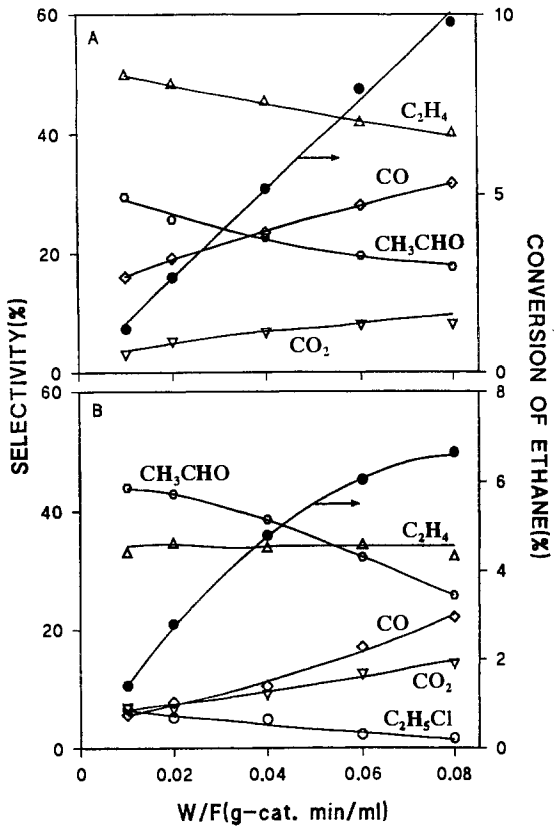

Fig. 4. Effect of contact time on ethane conversion and selectivity over 20 wt% HPMo/SiO_2 in the presence and absence of TCM: $C_2H_6/N_2O = 4/1$. (A) $T_R = 540°C$, TCM absent, (B) $T_R = 450°C$, TCM present (0.2 mol% in the feed). Same symbols as in fig. 1.

presence of TCM, has been investigated on the 20% HPMo/SiO_2 catalyst (table 1). In the presence of TCM, the conversion of ethylene and the selectivity to acetaldehyde increased. Ethylene and a small amount of acetaldehyde were the main products from ethyl chloride.

4. Discussion

The introduction of TCM into the ethane feedstream increases the conversion of ethane while leaving the selectivities relatively unchanged. In contrast, the introduction of TCM to the methane feedstream generally increased both the conversion and selectivity to C_2 hydrocarbons, with many of the studied catalysts, although the contribution of ethylene to the selectivity was higher while that of ethane was lower with tetrachloromethane present than in its absence (see, for example, ref. [49]). Although the earlier work with methane and 12-tungstophosphoric acid, for example, showed that at low contact times high selectivities to methyl chloride were obtained, the selectivities to ethyl chloride found in the present work are invariably small for all conditions studied. The effect of TCM on the conversion of ethane to ethylene as observed in the present work shows that at least a part of the enhancement produced by TCM when present in the methane feedstream results from the increased ethane conversion. However, since the present work focuses on HPMo/SiO_2 extrapolation of the present results to other methane conversion catalysts must be done with caution.

The maximum in conversion of ethane which is observed at a loading of approximately 20 wt% HPMo

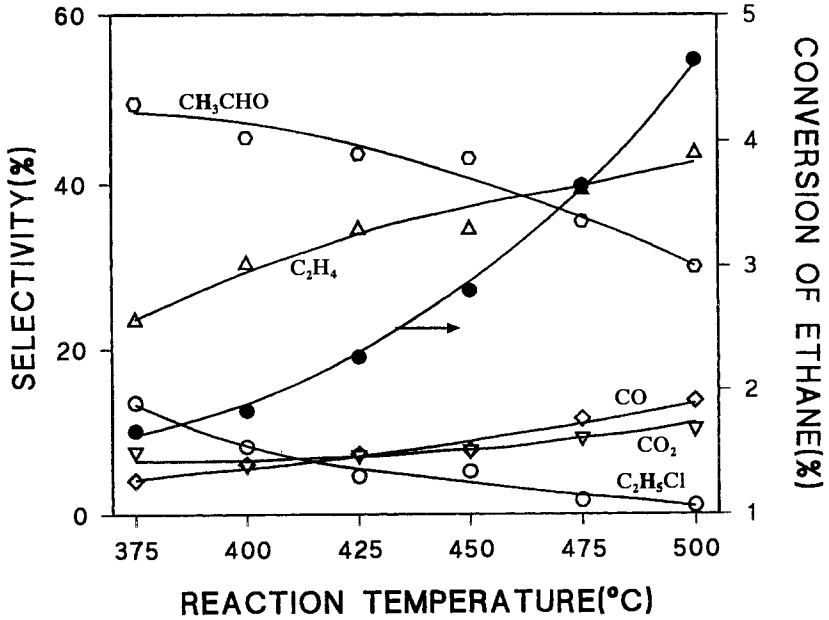

Fig. 5. Effect of reaction temperature on ethane conversion and selectivity over 20 wt% HPMo/SiO_2 in the presence of TCM (0.2 mol% in the feed): $W = 0.5$ g, $F = 25$ ml/min, $C_2H_6/N_2O = 4/1$. Same symbols as in fig. 1.

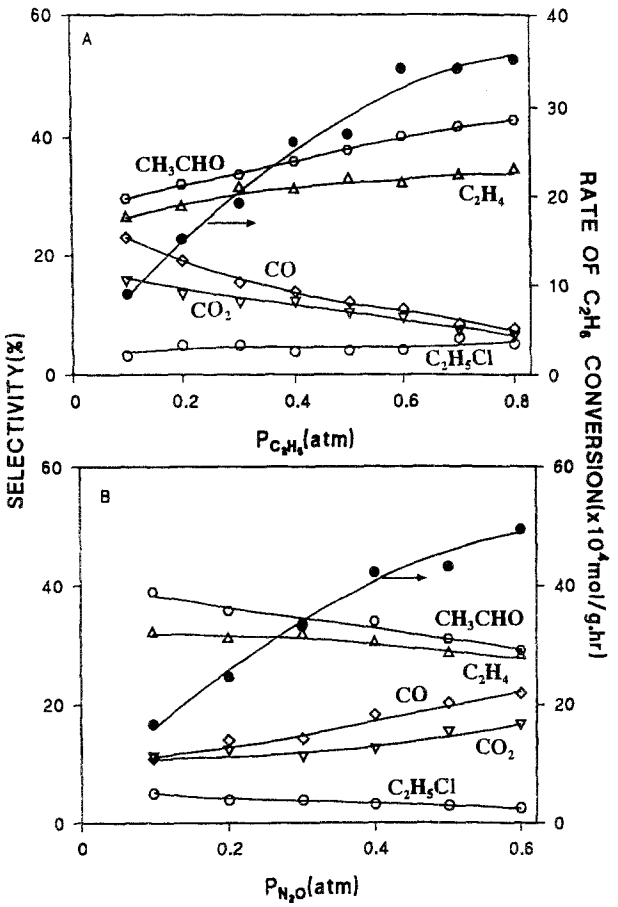

Fig. 6. Effect of partial pressure of C_2H_6 and N_2O on ethane conversion and selectivity over 20 wt% HPMo/SiO_2 in the presence of TCM (0.2 mol% in the feed): $T_R = 450°C$, $W = 0.5$ g, $F = 25$ ml/min. (A) $P_{N_2O} = 0.2$ atm, (B) $P_{C_2H_6} = 0.4$ atm. Same symbols as in fig. 1.

on SiO_2 is particularly significant. In the earlier work on the partial oxidation of methane the same loading was observed to produce optimum results [31]. It is interesting to note that, although, in the partial oxidation of methane on HPMo/SiO_2 catalysts the selectivity to methanol was small, nevertheless the maximum in this selectivity occurred at a loading of approximately 20 wt%. Since this corresponds to a coverage of approximately 1000 Å^2 per anion, to be compared with the anion cross-sectional area of 100 Å^2, each anion is expected to be isolated on the support surface.

Although ethane displays a continuous increase in conversion with increase in reaction temperature up to 500°C the selectivity to acetaldehyde appears to suffer large decreases for temperatures above approximately 450°C. In the earlier work on methane catalyst pretreatment temperatures in excess of approximately 450°C lead to decreases in the conversion of methane and in the selectivity to formaldehyde. Since bulk HPMo is known to be decomposed at 340–350°C [50], the silica support is apparently providing a thermal stabilization of the supported HPMo. Infrared, Raman, XPS and ^{31}P NMR studies have provided additional evidence for this enhanced thermal stability [42–45]. The XPS data also show that the anions of HPMo can be deposited uniformly on the silica surface in a highly dispersed form up to a coverage of about 0.04 anion nm^{-2}. For loadings greater than approximately 0.12 anion nm^{-2} particles of HPMo begin to form on the silica support. Both laser Raman and ^{31}P NMR spectroscopic results show that the highly dispersed HPMo is stable up to pretreatment or reaction temperatures of approximately 580–600°C. In contrast, laser Raman spectra show that the particles of HPMo present on the highly loaded catalysts are converted to MoO_3 at temperatures considerably lower than 580°C.

The conversion of ethane appears to be dependent on, among other factors, the presence of the heteropoly anion in a form which is accessible to the ethane. Although earlier photoacoustic FTIR work has shown that polar molecules can penetrate into the bulk structure of the metal–oxygen cluster compounds, that is, between the cations and anions [51] non-polar molecules such as ethane are unable to do so and the availability of the anion must be facilitated by depositing the 12-molybdophosphoric acid on a suitable high area support, particularly since the surface area of HPMo in unsupported form is quite small (< 10 m^2 g^{-1}). Loadings of approximately 20 wt% with which each HPMo is accessible to the ethane molecules are evidently ideal, whereas higher loadings which lead to particulate formations of HPMo on the silica would render significant amounts of the catalyst inaccessible to ethane molecules.

Table 1
Conversion and selectivity of C_2H_4 and C_2H_5Cl over HPMo/SiO_2 (20 wt%) [a]

Reactant composition	Conversion (%)	Selectivity (%)				
		CO	CO_2	C_2H_4	CH_3CHO	C_2H_5Cl
C_2H_4 (50%) + N_2O (50%) [b]	4.80	40.0	29.1	–	13.3	–
C_2H_4 (50%) + N_2O (50%) [c]	4.23	23.6	18.4	–	54.9	1.3
C_2H_5Cl (50%) + N_2O (50%) [d]	11.81	3.8	2.4	73.0	20.0	–

[a] Reaction conditions: $W = 0.5$ g, $F = 25$ ml/min, $T_R = 450°C$ ([b] 540°C).
[b] Small amount of ethane and methane was formed, TCM absent.
[c] TCM present, 0.2 mol% in the feed.
[d] TCM absent.

The trends in the selectivities observed with decreasing contact time strongly suggest that ethylene, acetaldehyde and ethyl chloride (where TCM is present in the feedstream) are primary products. The introduction of increasing, yet small, quantities of TCM into the ethane feedstream has relatively little influence on the selectivities of the first two of the aforementioned compounds, while increasing the conversion significantly. In addition, the presence of the heteropoly anion appears to be important for the production of acetaldehyde.

In their studies of ethane conversion on silica-supported alkali molybdate catalysts, Erdöhelyi, Mate and Solymosi [24] have suggested that the molybdenum in the 5+ oxidation state reduces N_2O to N_2 while itself being oxidized as

$$Mo^{5+} + N_2O \rightarrow Mo^{6+}-O^- + N_2 \quad (1)$$

A similar process may be occurring in the case of 12-molybdophosphoric acid. The earlier work on the partial oxidation of methane on HPMo/SiO_2 provided evidence for the indirect participation of the protons in the oxidation process [38,40]. Substitution of the protons by other cations, for example, cesium, reduced the catalytic activity. Further, temperature-programmed desorption experiments coupled with those from photoacoustic FTIR spectroscopy showed that at temperatures of 300–400°C water was associatively desorbed from the catalyst suggesting that protons had extracted oxygen from the anions leaving an oxygen vacancy on the anion which is apparently charged, thus resembling an F-center, which has recently been proposed by Goodman and coworkers as the active centre in the methane conversion process [52]. The production of such a vacancy would lead to the reduction of a molybdenum atom in the anion from the 6+ to the 5+ oxidation state. The contrast in the results obtained with the two oxidants N_2O and O_2 may thus be related to the inability of the dioxygen to oxidize the Mo^{5+} when it is bound in the HPMo anion, that is, to fill the oxygen vacancy in the anion.

While the Keggin anion appears to be important in the formation of acetaldehyde, the conversion of ethane, and not the selectivities, is apparently enhanced by introduction of tetrachloromethane. Since there is considerable evidence to support the contention that oxidation processes proceed through radical mechanisms [16,53] it is tempting to conclude that the participation of TCM is restricted to the enhancement of $C_2H_5\cdot$ production. Indeed, the homogeneous reaction of alkanes with carbon tetrachloride proceeds through a free radical chain mechanism in both the gas and solution phases [54–60] so that, for ethane, stoichiometric reactions such as

$$C_2H_5\cdot + CCl_4 \rightarrow C_2H_5Cl + \dot{C}Cl_3$$

$$C_2H_6 + \dot{C}Cl_3 \rightarrow C_2H_5\cdot + HCCl_3$$

can be hypothesized. Such a mechanism would account for the formation of ethyl chloride as well as ethyl radicals. However, since the selectivity to acetaldehyde from the oxidation of ethylene with N_2O is increased by a factor of four on addition of 0.2 mol% TCM (table 1), the direct involvement of TCM in the production of acetaldehyde from ethane cannot be ruled out.

Finally it should be noted that earlier work on the partial oxidation and oxidative coupling of methane on silica-supported HPW and HPMo has shown that pretreatment of the catalyst with TCM followed by reaction in the absence of TCM produces results which are similar to those found with TCM present in the methane feedstream [46–48]. Similar observations have been made with other catalysts (see, for example, ref. [37]). Although the aforementioned experiments provide evidence for the interaction of chlorine with the surface (and possibly bulk) of the catalyst and the involvement of the chlorine-containing surface species in the catalytic process, the participation of TCM in the gas phase cannot be ruled out.

Acknowledgement

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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