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THE CONVERSION OF METHANE ON HETEROPOLY OXOMETALATES IN THE PRESENCE OF TETRACHLOROMETHANE

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The addition of a small amount of tetrachloromethane to the reactant stream in the conversion of methane by nitrous oxide increases the yield of partial oxidation product formaldehyde over silica-supported 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$), but selectively produces monochloromethane over silica-supported 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$).

There is currently considerable interest in the direct conversion of methane to petrochemical feedstocks and liquid fuels on heterogeneous catalysts [1–4]. Much of the work has focussed on the partial oxidation of methane with nitrous oxide to produce formaldehyde and methanol on a variety of oxides, such as those of silica-supported molybdenum and vanadium [5,6], on Bi_2O_3–SnO_2 [7] and on Fe ZSM 5 [8], and to higher hydrocarbons with oxygen on transition metal oxides [9]. Research in this laboratory on the oxidation of methane has employed various heteropoly oxometales [10–13] and halogenated mordenite [14]. Chlorination and oxychlorination [1,15,16] have also been employed as processes for the conversion of methane. Attempts have also been made to combine oxychlorination and conversion of hydrocarbons with dual-function catalysts such as cupric chloride and H-ZSM-5 [17].

While the beneficial effects of the addition of relatively small quantities of halogens and halogenated compounds are well documented for processes such as the reforming of naphtha on alumina-supported platinum catalysts [18] and the oxidation of ethylene to ethylene oxide over supported silver catalysts [19], there are relatively few reports on the use of these additives in the literature on the oxidation of methane [20,21] and these have been with supported metal catalysts.

Earlier work in this laboratory has shown that 12-molybdophosphoric acid supported on silica is an effective catalyst for the selective oxidation of methane by nitrous oxide and oxygen [10–12]. It has also been shown that silica itself is active in the oxidation process [13]. The present communication demonstrates that the addition of a small quantity of tetrachloromethane to the feed strikingly alters the activity and selectivity in the conversion of methane by nitrous oxide on the two heteropoly oxometalates, 12-molybdophosphoric (HPMo) and 12-tungstophosphoric (HPW) acids supported on silica.

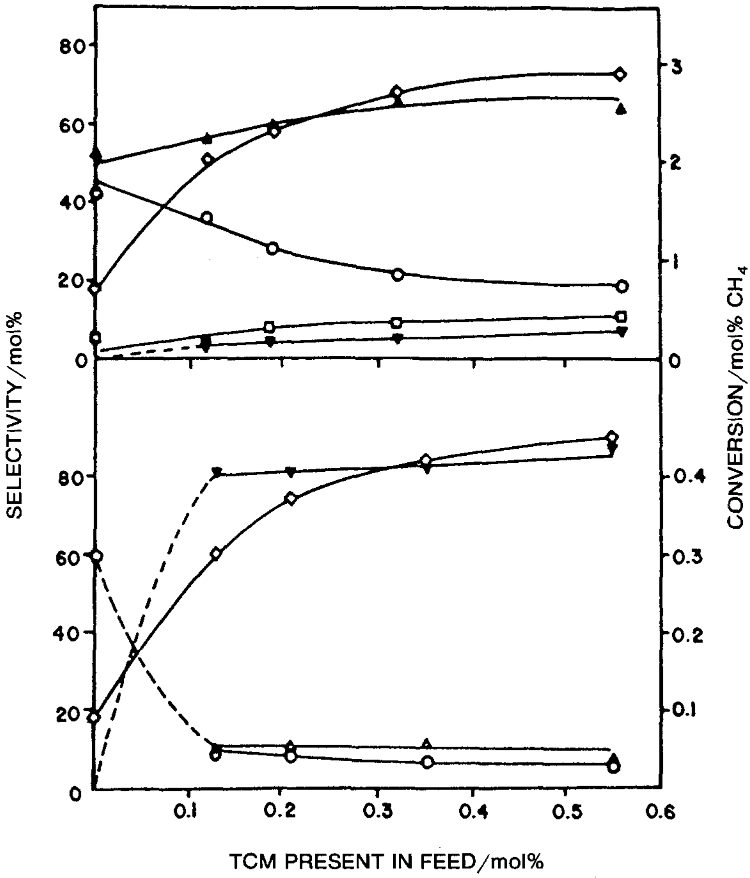

Fig. 1. Conversion and selectivity as a function of concentration of TCM in the feed ($T = 450\,^{\circ}$C). a. HPMo/SiO_2 $W = 1.05$ g, $F = 60$ ml min^{-1}, $CH_4/N_2O \approx 1$; b. HPW/SiO_2 $W = 2.0$ g, $F = 60$ ml min^{-1}, $CH_4/N_2O \approx 4$. Selectivities: ○ H_2CO, △ CO_2, □ CO_2, ▽ CH_3Cl, ◇: conversion [(products/methane fed)(×100)]

The reaction was studied in a fixed bed continuous flow reactor operating near atmospheric pressure. The additive was introduced into the main flow of CH_4 and N_2O by bubbling helium through a saturator containing the liquid at ice-water temperature. The catalysts were prepared by impregnation of the silica (Grace-Davison grade 407, 8–20 mesh) with an aqueous solution of HPMo or HPW (20% by wt.) by an incipient wetness technique and were dried at about 80 °C for several hours. The calcination was performed in situ in the pyrex reactor at the temperature of reaction (450 °C) immediately prior to the reaction. The reactants and products were analyzed by gas chromatography.

Figure 1 summarizes the effect of tetrachloromethane (TCM) on the oxidation of methane by N_2O on 12-molybdophosphoric acid and 12-tungstophosphoric acid supported on silica. The conversion on both of these catalysts is strikingly augmented by the introduction of TCM and the increase is most pronounced with smaller additions of TCM.

On each of the catalysts, in addition to the usual oxidation products, monochloromethane is produced in significant amounts. Interestingly, however, the relative proportions of oxidation products and monochloromethane are remarkably different over the two catalysts. While on HPMo/SiO_2 oxidation products account for the major portion of methane reacted, on HPW/SiO_2 monochloromethane accounts for more than 80% of methane reacted. On HPMo/SiO_2, although the selectivity to the partial oxidation product H_2CO decreases with the increasing concentration of TCM, the overall yield of H_2CO (sel. × conv.) is substantially increased in the presence of TCM, reflecting the advantageous effect of the introduction of TCM in the feed. On HPW/SiO_2, additions of TCM drastically alter the selectivities compared to those in its absence, but the actual amount of TCM present in the feed has little effect on the selectivity although the conversion slightly increases with increasing concentration of TCM. When N_2O was excluded from the feed (replaced by an equal flow of helium), conversion dropped by several-fold over each of the catalysts, indicating that N_2O plays a vital role in the reaction.

Experiments conducted over the bare support showed that the support itself was much less active than when loaded with the heteropoly compound. In the absence of the catalyst, with the concentrations of TCM, CH_4 and N_2O and flow rates employed, the conversion of methane was insignificant. However, TCM itself, underwent oxidation to a substantial extent on each of the catalysts and the product was exclusively CO_2. The results shown in the figure have been corrected for this. (On HPW/SiO_2, the rate of formation of CO_2 was very similar with or without the presence of CH_4 in the feed, and therefore, was ignored in the calculation of selectivities.)

The effect of residence time on conversion and selectivity in the presence and absence of the additive is shown in fig. 2 for two catalysts. Where the additive is present suitable correction for TCM oxidation has been made. It is clearly evident that on each of the catalysts, the conversion of methane is substantially higher when CCl_4 is present in the feed over the entire range of residence time investigated. While in the absence of CCl_4 the conversion of methane increases linearly with W/F in its presence the increase in conversion is somewhat slower at longer W/F's on both the catalysts, particularly on HPW/SiO_2. On HPMo, selectivity to H_2CO is similar in the presence and absence of CCl_4 at longer contact times in spite of much higher conversion of methane when the additive is present, demonstrating the beneficial effect of the introduction of halogenated species in the CH_4/N_2O feed. On HPMo/SiO_2, as the residence time is reduced, the selectivity to H_2CO rapidly increased in the absence of CCl_4. This increase in the H_2CO selectivity was almost exclusively at the expense of CO selectivity indicating that CO was produced by the subsequent degradation of H_2CO. However, in the presence of CCl_4, the fact that selectivity to H_2CO does not

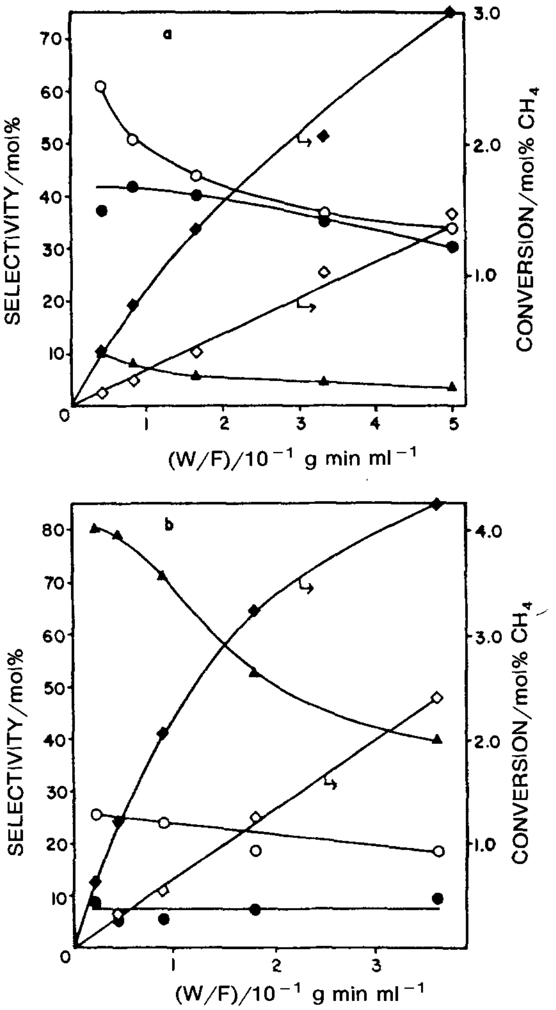

Fig. 2. Conversion and selectivity as a function of residence time (W/F) in the presence and absence of CCl_4 in the feed ($T = 450\,^{\circ}C$, $W = 0.25$ g–4.0 g). a. $HPMo/SiO_2$, $[CCl_4]_{fed} = 0.17\%$ (by mole), $F = 60$ ml min^{-1}, $CH_4/N_2O \approx 4$; b. HPW/SiO_2, $[CCl_4]_{fed} = 0.38\%$ (by mole), $F = 11$ ml min^{-1}, $CH_4/N_2O \approx 1$. Filled symbols: CCl_4 present, Open symbols: CCl_4 absent ◇, ◆ conversion [(products/methane fed)(×100)]; ▲ CH_3Cl; ○, ● H_2CO (balance $CO+CO_2$ omitted for clarity)

increase further at relatively small residence times suggests that there is a parallel and independent path for the production of CO in addition to that from H_2CO. On HPW/SiO_2, it is observed that, unlike that on $HPMo/SiO_2$, the selectivity to H_2CO is relatively constant with contact time regardless of the presence of the additive. A similar result was also observed at 525 °C. This suggests that on HPW/SiO_2, the partial and deep oxidation products are produced by independent paths. On HPW/SiO_2 the conversion of methane to oxygenated products increased linearly with residence time, but, in the presence of CCl_4, conversion of methane to CH_3Cl reached a saturation point after an initial increase. This may account for the apparent non-linearity in the conversion in the presence of CCl_4 on HPW/SiO_2.

The pretreatment of the catalyst with the additive, followed by reaction with the feed consisting of CH_4/N_2O only (no CCl_4), also had the effect of substantially increasing the conversion of CH_4 on both the catalysts, but the effect, as expected, was short-lived in terms of time on stream. Re-introduction of the additive to the feed restored the high activity of the catalyst.

From the results described above it appears that HPMo/SiO_2, in the presence of CCl_4, behaves primarily as an oxidation catalyst, similar to that in its absence [10–12]. On the other hand, HPW/SiO_2 which is found to be a relatively poor oxidation catalyst both in terms of conversion of CH_4 and selectivity to liquid product(s) [10] behaves as an effective oxychlorination catalyst when a small quantity of TCM is introduced in the feed. Evidently, it was possible to obtain a selectivity to monochloromethane of ~ 60% at a methane conversion of about 3% (fig. 2). It is remarkable that the specific selectivity to monochloromethane approaches 100% while other chloromethanes, di- or tri-, are, at most, produced in trace quantities. While N_2O is expected to provide an oxygen source for the production of oxygenates on HPMo/SiO_2, its function in the formation of CH_3Cl on HPW/SiO_2 is less evident. In the case of oxychlorination process on cupric chloride catalyst, it is suggested that the function of oxygen is to reoxidize ($CuCl \rightarrow CuCl_2$) the catalyst after reduction in the chlorination process [15]. Although confirming data is not yet available with the present catalysts, a similar rationalization may be possible here.

Acknowledgements

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