

## An *in Situ* XRD Investigation of Singly and Doubly Promoted Manganese Oxide Methane Coupling Catalysts

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*In situ* X-ray diffraction (XRD) and concurrent measurements of catalytic performance have been used to characterise the solid phases present during various stages in the history of working methane coupling catalytic systems. Three such systems were studied: unpromoted, K-promoted, and KCl-promoted manganese oxide. In each case the effect of pulses of  $\text{CHCl}_3$  on the activity, selectivity, and catalyst structure was determined. Depending on the conditions, various oxides or mixed oxides of Mn were present. Of these,  $\text{Mn}_3\text{O}_4$  is an unselective total oxidation catalyst; K-promotion stabilises this phase, drastically reducing  $\text{CO}_2$  formation and raising  $\text{C}_2$  activity. Chloride ions (added as KCl) prevent the formation of highly unselective potassium manganese oxides. Chlorine introduced from the gas phase has an additional effect:  $\text{C}_2$  activity is further enhanced leaving  $\text{CO}_2$  production unaffected. This form of chlorine promotion is greatly augmented by the presence of KCl. There are strong indications that the effects of chlorine involved substantial modification of the surface chemistry and are not purely due to Cl atom-induced homogeneous chemistry. © 1992 Academic Press, Inc.

### INTRODUCTION

Oxidative coupling of methane is currently the subject of much academic and industrial research, the early work of Keller and Bhasin (1) having demonstrated that a wide range of metal oxides exhibit useful activity for this reaction. Since then, a very large number of oxides have been screened for catalytic activity, including materials which can exhibit redox behaviour under reaction conditions. An important example of this latter class is provided by the oxides of manganese (2-5) and of particular relevance to the present work are the promotional effects of potassium and chlorine on such systems. Burch *et al.* (4, 6) have shown that the introduction of chlorine containing compounds from the *gas phase* greatly in-

creases the selectivity towards  $\text{C}_2$  formation with such manganese oxide catalysts. They suggest that this is due to promoter-induced formation of an  $\text{Mn}_3\text{O}_4$ -like phase; furthermore they demonstrated that the active chlorine modified phase is unstable in the absence of potassium. The various phases were identified using *ex situ* XPS and XRD, carried out on quenched catalyst samples. More recently, Bradshaw and co-workers (7) have tested a range of *alkali halide*-promoted manganese oxide catalysts, finding that in all cases injection of gaseous  $\text{CHCl}_3$  resulted in a switch from total oxidation of  $\text{CH}_4$  to high selectivity for  $\text{C}_2$  formation (up to around 80%). KCl was found to be the most effective alkali halide promoter, the results indicating that the role of the alkali halides was to enhance and extend the promotional effect resulting from gas phase chlorocompound injection. The authors suggested that chlorine be-

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comes part of an active centre for oxidative coupling and is not merely a poison for total oxidation.

Recently, we have carried out an electron spectroscopic investigation of a doubly promoted ( $\text{K(s)} + \text{Cl}_2(\text{g})$ ) model planar  $\text{Mn}_3\text{O}_4$  catalyst (8). It was found that the presence of both chlorine and potassium was necessary for the formation of a new oxygen-containing surface phase, an observation which appeared to be consistent with the synergistic effects reported (6, 7) for doubly promoted practical manganese oxide catalysts. It seems clear that potassium and chlorine (derived from both solid ionic and gaseous compounds) show interesting promotional effects on manganese oxides, the exact nature of which requires further investigation. In particular, the role of the phases of manganese oxide present under reaction conditions is critical and has to date been unclear.

The present paper describes the results of a study in which *in situ* XRD coupled with *concurrent* activity and selectivity measurements have been used to characterise the solid phases present during oxidative methane coupling using a series of related manganese oxide catalysts. In particular, we have tried to elucidate the roles played by potassium promotion, promotion by "solid state" chlorine (KCl) and by introduction of chlorine from the gas phase ( $\text{CHCl}_3$ ). Three systems were studied, namely unpromoted, potassium-promoted, and potassium chloride-promoted manganese oxide. In each case the effect of pulses of  $\text{CHCl}_3$  on the activity, selectivity, and structure of the catalyst was determined.

## EXPERIMENTAL

### Sample Preparation

$\text{MnO}_2$  (Aldrich 99.99%) was used as the starting material for all catalysts. It was used untreated as the unpromoted manganese oxide sample, and XRD confirmed that  $\text{MnO}_2$  was the only phase present in this material. The potassium chloride-promoted manganese oxide was prepared by calcining intimately ground 25 wt.% KCl/ $\text{MnO}_2$  for 10 h

at 750°C; XRD analysis showed the presence of  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}(\text{OH})_4$ , and KCl in the proportions 3.0:3.7:1.0. Potassium-promoted manganese oxide was prepared so that the same mole fraction of potassium was present as in the potassium chloride promoted material. Intimately ground  $\text{K}_2\text{CO}_3/\text{MnO}_2$  was calcined for 20 h at 750°C. XRD analysis showed  $\text{KMn}_8\text{O}_{16}$  to be the only phase present after this procedure.

Unless otherwise stated, these three materials were used as the starting materials for experiments on the unpromoted, potassium chloride-promoted, and potassium promoted-catalysts, respectively.  $\text{Mn}_3\text{O}_4$  was prepared from  $\text{MnO}_2$  by decomposition in air at 1000°C for 20 h.

### Apparatus and Method

The experiments described below were carried out in a specially designed *in situ* X-ray diffraction cell, a schematic diagram of which is shown in Fig. 1. An 18%  $\text{CH}_4$ /3%  $\text{O}_2$ /balance He gas mixture (BOC) was passed through the cell while XRD patterns were collected using a Siemens D500 diffractometer. XRD patterns were assigned using the JCPDS database (9). XRD scans were taken over 1 h each and concurrent gas analysis of the exit gas was achieved by means of a Perkin Elmer Sigma 300 HWD gas chromatograph, equipped with an LCI100 integrator. Experiments were performed at 700°C and one atmosphere pressure. Unless otherwise stated, a flow rate of  $10 \text{ cm}^3/\text{min}^{-1}$  was used; flow rates of 20 and  $3 \text{ cm}^3/\text{min}^{-1}$  were also used for comparison purposes and the results of these experiments are summarised in Table 1. About 0.02 g of sample was used in every experiment, each of which was conducted over 10 h. Initially a 1-h scan of the cold starting material was performed; then the sample was heated and four further scans carried out, during which time the reaction reached steady state.  $5 \mu\text{l}$  of  $\text{CHCl}_3$  was injected between scans 5 and 6 and an additional five scans were then performed;  $5 \mu\text{l}$  of  $\text{CHCl}_3$  is equivalent to approximately one chlorine

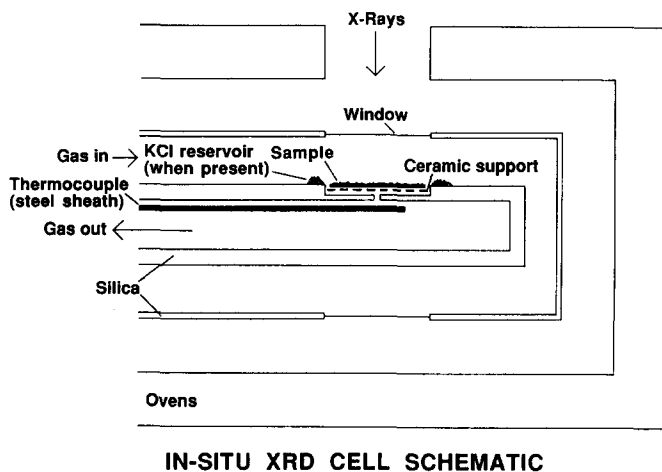


FIG. 1. Schematic drawing of *in situ* XRD cell.

atom per manganese ion present in the sample. The *average*  $\text{CHCl}_3:\text{CH}_4$  ratio was  $\sim 1:2000$  over the 5 h following injection.

A major problem in investigating the methane-oxygen mixtures will react over hot stainless steel surfaces to form carbon oxides. Thus a crucial feature of the cell used here is that all hot parts in contact with the gas mixture were made of silica, which is inert for this reaction. The only exception to this was the thermocouple, which was encased in inconel steel; it was situated below the sample as shown in Fig. 1. This location was downstream of the catalyst bed so that any reactions catalysed by the thermocouple sheath could not affect the environment of the catalyst. Hence it can be stated with confidence that the X-ray diffraction patterns refer to working catalysts in a true reaction environment. However, reactions due to the thermocouple sheath would have some effect on the observed product distributions. Control experiments with  $\text{CH}_4$  performed in the absence of catalyst showed only a small level of carbon oxides formation: about 0.15 vol% in the output stream, mainly  $\text{CO}_2$ . In the full working system the catalyst depletes some of the oxygen so that the level of background reac-

tion is reduced further. A more serious problem arises because combustion of the  $\text{C}_2$  products is efficiently catalysed by steel surfaces. Control experiments in which  $\text{C}_2\text{H}_6/\text{O}_2$  or  $\text{C}_2\text{H}_4/\text{O}_2$  mixtures were fed through the cell showed very high activities for carbon oxide formation, in particular CO. It is very difficult to quantify the effect of this as it is highly dependent on the gas composition at the thermocouple. It can, however, be confidently asserted that the product distributions observed were substantially worse than those actually achieved immediately downstream of the catalyst bed, due to the spurious combustion of reactant and (especially) product hydrocarbons; hence our results are consistent with the 80–90% selectivities achieved by Burch *et al.* (6) and Bradshaw and co-workers (7) using similar catalysts. As a result of this, the product distributions shown should be taken only as a qualitative indication of changes in catalyst performance, not a quantitatively accurate record of selectivities and yields.

#### RESULTS AND DISCUSSION

Figures 2–11 show the X-ray diffraction patterns and corresponding reaction data for the most revealing experiments. A summary of all phases present in these and other ex-

TABLE 1  
Summary of Solid Phases Present During *in situ* XRD Experiments

	MnO <sub>2</sub>	MnO <sub>2</sub> /K <sub>2</sub> CO <sub>3</sub> calcined	MnO <sub>2</sub> /KCl calcined
		3 cm <sup>3</sup> min <sup>-1</sup> 700°C	
Before CHCl <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub> + MnO	Mn <sub>3</sub> O <sub>4</sub> + K <sub>0.97</sub> Mn <sub>0.94</sub> O <sub>2</sub> + unknown	Mn <sub>2</sub> O <sub>3</sub> + MnO <sub>2</sub> + KCl
After CHCl <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub> + MnO	Mn <sub>3</sub> O <sub>4</sub> + transient KCl	Mn <sub>3</sub> O <sub>4</sub> + KCl
		10 cm <sup>3</sup> min <sup>-1</sup> 700°C	
Before CHCl <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub> + Mn <sub>2</sub> O <sub>3</sub> → Mn <sub>3</sub> O <sub>4</sub> + MnO	K <sub>0.47</sub> Mn <sub>0.94</sub> O <sub>2</sub> + some KMn <sub>8</sub> O <sub>16</sub>	Mn <sub>2</sub> O <sub>3</sub> + KCl + MnO <sub>2</sub>
After CHCl <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub> + MnO	Mn <sub>3</sub> O <sub>4</sub> + transient KCl	Mn <sub>3</sub> O <sub>4</sub> + KCl + Traces Mn <sub>2</sub> O
		20 cm <sup>3</sup> min <sup>-1</sup> 700°C	
Before CHCl <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub>	K <sub>0.47</sub> Mn <sub>0.94</sub> O <sub>2</sub> + some KMn <sub>8</sub> O <sub>16</sub>	Mn <sub>2</sub> O <sub>3</sub> + MnO <sub>2</sub> + KCl
After CHCl <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub> + transient MnO	Mn <sub>3</sub> O <sub>4</sub>	Mn <sub>3</sub> O <sub>4</sub> + KCl + Traces Mn <sub>2</sub> O <sub>3</sub>
		10 cm <sup>3</sup> min <sup>-1</sup> 700°C	
Before CHCl <sub>3</sub>			Mn <sub>3</sub> O <sub>4</sub> /KCl
After CHCl <sub>3</sub>			Mn <sub>3</sub> O <sub>4</sub> + KCl Mn <sub>3</sub> O <sub>4</sub> + KCl
	MnO <sub>2</sub>		MnO <sub>2</sub> /KCl calcined
		10 cm <sup>3</sup> min <sup>-1</sup> 700°C	
Before CH <sub>3</sub> OH	Mn <sub>3</sub> O <sub>4</sub> + Mn <sub>2</sub> O <sub>3</sub> → Mn <sub>3</sub> O <sub>4</sub> + MnO		Mn <sub>2</sub> O <sub>3</sub> + MnO <sub>2</sub> + KCl
After CH <sub>3</sub> OH	Mn <sub>3</sub> O <sub>4</sub> + MnO		Mn <sub>3</sub> O <sub>4</sub> + KCl

periments is shown in Table 1. Figures 2 and 3 refer to unpromoted manganese oxide; a mixture of Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>2</sub>O<sub>3</sub> formed initially, undergoing reduction to Mn<sub>3</sub>O<sub>4</sub> and traces of MnO over 3–4 h. On injection of CHCl<sub>3</sub> the proportion of MnO present increased initially but then decreased again, though never returning to the level present before the CHCl<sub>3</sub> pulse. Thus the pulse of CHCl<sub>3</sub> results in some reduction of the manganese oxide. The reaction data in Fig. 3 show complete oxygen consumption and extremely high selectivity towards CO<sub>2</sub> throughout, with the exception of the period immediately following CHCl<sub>3</sub> injection; this is consistent with known homogeneous gas phase chlorine chemistry (10). Thus the gas-

eous chlorine precursors appear to be ineffective in promoting otherwise unpromoted manganese oxide. Inspection of Table 1 shows that catalyst reduction following CHCl<sub>3</sub> injection is observed in all systems (with the exception of KCl promoted Mn<sub>3</sub>O<sub>4</sub>), usually to a greater extent than seen in this particular case. It is interesting to note that this effect was generally accompanied by a drop in oxygen consumption (see Figs. 5 and 7); thus more oxidising gaseous conditions arise following CHCl<sub>3</sub> injection and these correspond to the appearance of more reduced phases of manganese oxide. Clearly the pulse itself is altering the phase of manganese oxide present in an irreversible manner; the reason for this will be dis-

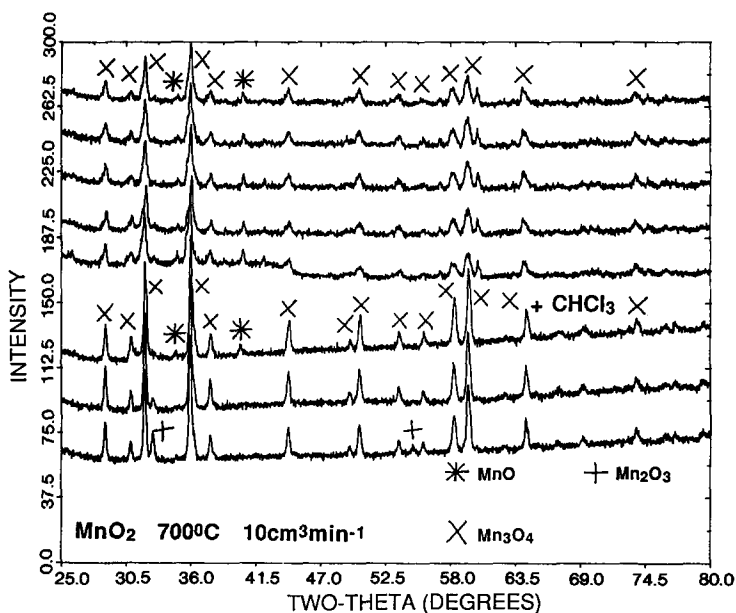


FIG. 2.  $\text{MnO}_2$ ,  $700^\circ\text{C}$ , gas flow rate  $10\text{ cm}^3\text{ min}^{-1}$ . XRD patterns recorded sequentially over 1 h each, starting 1 h after onset of heating.  $5\ \mu\text{L CHCl}_3$  injected after third scan.

cussed later. Note that a small unassigned peak at about  $2\theta = 60^\circ$  is visible in Fig. 2; this appears only after injection of  $\text{CHCl}_3$ . The peak could not be matched to any of the JCPDS database patterns for manganese

oxides, carbonates or chlorides. It appeared only occasionally and is most likely due to deposition of a compound of manganese (possibly chloride or oxychloride) on the X-ray window.

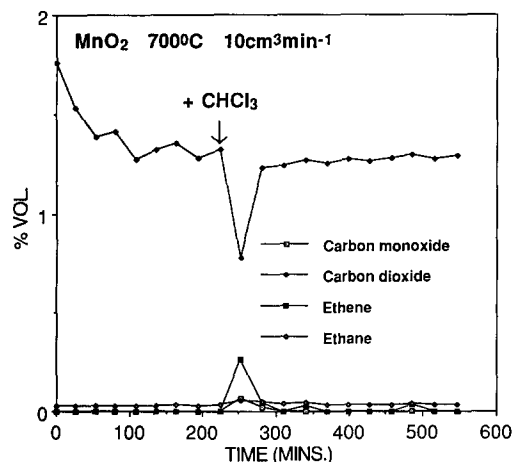


FIG. 3.  $\text{MnO}_2$ ,  $700^\circ\text{C}$ , gas flow rate  $10\text{ cm}^3\text{ min}^{-1}$ . Reaction data acquired simultaneously with the XRD patterns of Fig. 2.

Figure 4 illustrates an experiment on potassium-promoted manganese oxide. It is evident that with potassium promotion alone, the stable phases are potassium manganese oxides ( $\text{K}_{0.47}\text{Mn}_{0.94}\text{O}_2$  and  $\text{KMn}_8\text{O}_{16}$ ). On injection of  $\text{CHCl}_3$  potassium is extracted to form  $\text{KCl}$  and the manganese is left in the form of  $\text{Mn}_3\text{O}_4$ . Figure 5 shows the corresponding reaction data. From these results it is obvious that the potassium manganese oxide phases are excellent total oxidation catalysts. However, following  $\text{CHCl}_3$  injection, on formation of a  $\text{KCl}$  promoted  $\text{Mn}_3\text{O}_4$  phase, good  $\text{C}_2$  selectivity is obtained. This is particularly noticeable for the period  $\sim 1.5\text{--}3.5$  h after injection; loss of selectivity after this is almost certainly due to evaporation of  $\text{KCl}$  from the catalyst bed. Indeed, condensed  $\text{KCl}$  was found downstream of the catalyst after the experiment

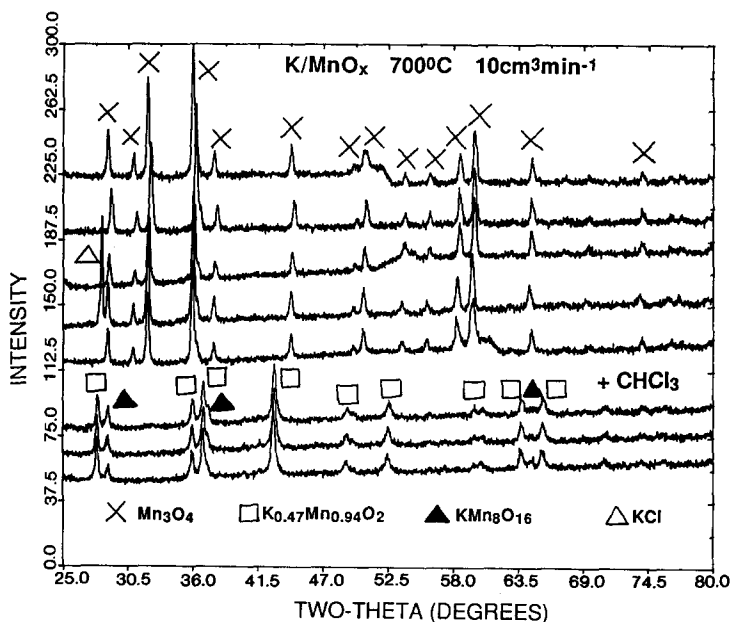


FIG. 4.  $K_2CO/MnO_2$  (calcined),  $700^\circ C$ , gas flow rate  $10\text{ cm}^3\text{ min}^{-1}$ . XRD patterns recorded sequentially over 1 h each, starting 1 h after onset of heating.  $5\ \mu\text{L CHCl}_3$  injected after third scan.

and the KCl in the XRD pattern was seen only transiently. Catalysts with lower K loadings ( $<5\%$ ) showed no improvement in selectivity (before  $CHCl_3$  injection) over the higher K loadings exemplified by the present

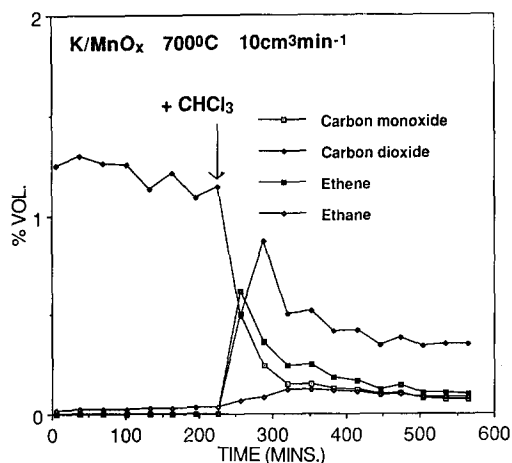


FIG. 5.  $K_2CO_3/MnO_2$  (calcined),  $700^\circ C$ , gas flow rate  $10\text{ cm}^3\text{ min}^{-1}$ . Reaction data acquired simultaneously with XRD patterns of Fig. 4.

data. Thus the improved selectivity does indeed seem to depend on the presence of KCl in the catalyst and is not merely the result of leaching out of potassium by KCl formation after  $CHCl_3$  injection. The oxidation state of manganese in the potassium manganese oxides is greater than 3, whereas for  $Mn_3O_4$  it is  $8/3$ . Clearly potassium promotes a more oxidised form of manganese (before  $CHCl_3$  injection) relative to the non-alkali-promoted system. Inspection of Table 1 shows that in all cases where potassium is present (either as KCl or as potassium alone) the oxidation state of manganese is higher before  $CHCl_3$  injection than for the corresponding non-alkali promoted system. It is also noticeable that when potassium is present, the oxidation state of manganese has much less tendency to vary than it does in the absence of potassium.

To investigate the steady state properties of KCl-promoted manganese oxide, a reservoir of KCl was provided adjacent to the catalyst bed so that the sample was continuously supplied with KCl vapour thus off-

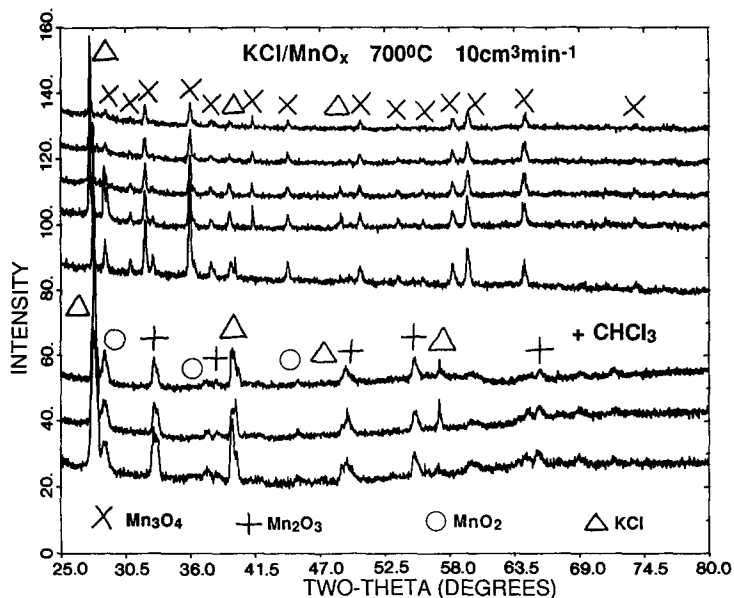


FIG. 6. KCl/MnO<sub>2</sub> (calcined) + KCl reservoir, 700°C, gas flow rate 10 cm<sup>3</sup> min<sup>-1</sup>. XRD patterns recorded sequentially over 1 h each, starting 1 h after onset of heating. 5 μL CHCl<sub>3</sub> injected after third scan.

setting KCl depletion. (Our reactor studies (11) have shown that a pure manganese oxide catalyst can be promoted by simply placing KCl upstream of the catalyst in the reactor hot zone. KCl depletion at reaction temperature is therefore believed to be a significant process.) Figure 6 shows the XRD patterns obtained in such an experiment. Once again CHCl<sub>3</sub> injection leads to catalyst reduction from Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> to Mn<sub>3</sub>O<sub>4</sub>. The corresponding reaction data (Fig. 7) show the sample to be a good combustion catalyst before the CHCl<sub>3</sub> pulse, though the C<sub>2</sub> yield was somewhat higher than for wholly unpromoted or K-promoted catalysts. However, following the CHCl<sub>3</sub> pulse good steady state C<sub>2</sub> selectivity was obtained (ethylene/ethane ~ 1.5), comparable to the short term effect observed in the K-promoted system following CHCl<sub>3</sub> injection. Thus KCl promotion raises C<sub>2</sub> selectivity principally by enhancing ethene production and decreasing CO<sub>2</sub> production; best results are obtained following CHCl<sub>3</sub> injection if KCl is also present. The presence of

chlorine appears to be necessary in order to prevent formation of an unselective potassium manganate phase, while the potassium seems to stabilise higher oxidation states of manganese. This latter promotional

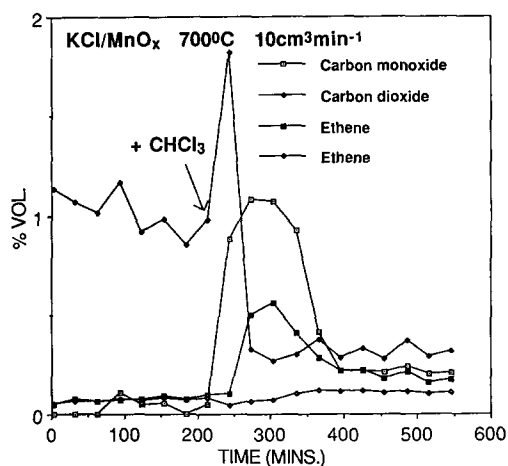


FIG. 7. KCl/MnO<sub>2</sub> (calcined) + KCl reservoir, 700°C, gas flow rate 10 cm<sup>3</sup> min<sup>-1</sup>. Reaction data acquired simultaneously with XRD patterns of Fig. 6.

effect is understandable for such catalysts which activate methane via a redox cycle: K-promotion could facilitate the regeneration of active surface sites following the initial hydrogen abstraction. In all cases  $\text{Mn}_3\text{O}_4$  is both the most stable and most selective phase under reaction conditions. However, a pulse of gas phase  $\text{CHCl}_3$  may be required to force the catalyst into adopting this phase. Two points remain unclear. First, whether the change of phase is related to the presence of gas phase chlorine or is simply a result of the transient reducing conditions produced by the combustion of the chloro-carbon. Second whether the improvement in catalytic performance following the  $\text{CHCl}_3$  pulse is merely a result of the phase change produced or whether chlorine from this source in fact has a direct heterogeneous catalytic role, e.g., by modifying active sites or providing active chlorine radicals on the catalyst surface. Two experiments to investigate these questions are now described.

To simulate the reducing conditions produced by the combustion of the injected pulse, but without the attendant gas phase chlorine,  $\text{CH}_3\text{OH}$  was injected instead of  $\text{CHCl}_3$ . Figure 8 shows the resulting XRD patterns for a KCl-promoted catalyst (with KCl reservoir) and comparison with Fig. 6 at once indicates that identical phase changes occur in the two cases. Table 1 shows an analogous result for the unpromoted system. Thus the presence of chlorine is clearly irrelevant to the formation of  $\text{Mn}_3\text{O}_4$ , this phase being produced by the transient presence of strongly reducing conditions and then being stable under more oxidising reaction conditions. Figure 9 shows the large drop in  $\text{CO}_2$  production attendant upon the formation of the  $\text{Mn}_3\text{O}_4$  phase, following  $\text{CH}_3\text{OH}$  injection; again, the behaviour is comparable to that observed on  $\text{CHCl}_3$  injection. However, no increase in  $\text{C}_2$  production is observed, in contrast to the case of  $\text{CHCl}_3$  injection. Therefore promotion with chlorine via the gas phase must have a role

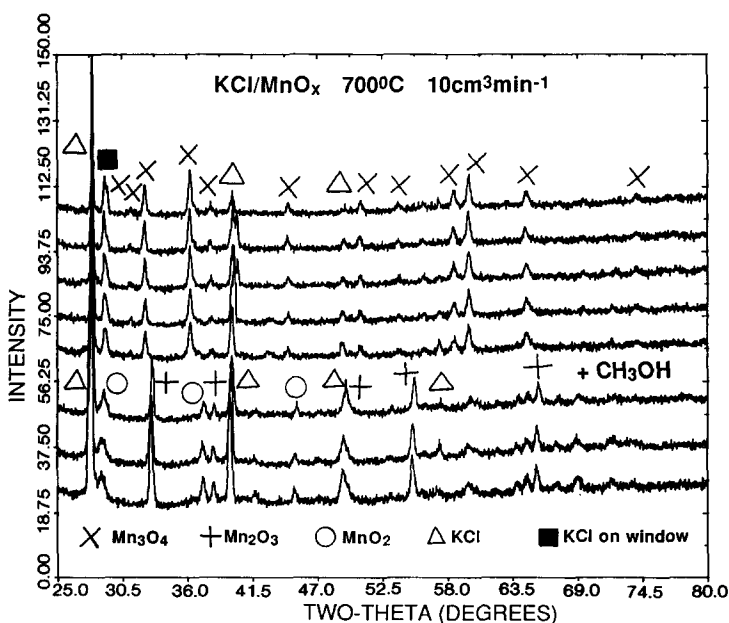


FIG. 8. KCl/MnO<sub>2</sub> (calcined) + KCl reservoir, 700°C, gas flow rate 10 cm<sup>3</sup> min<sup>-1</sup>. XRD patterns recorded sequentially over 1 h each, starting 1 h after onset of heating. 5 μL CH<sub>3</sub>OH injected after third scan.



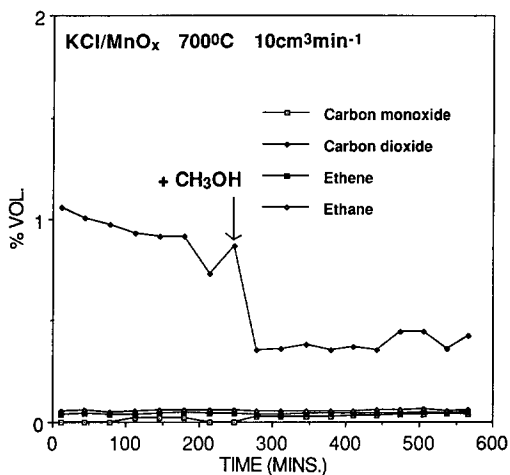


FIG. 9. KCl/MnO<sub>2</sub> (calcined) + KCl reservoir, 700°C, gas flow rate 10 cm<sup>3</sup> min<sup>-1</sup>. Reaction data acquired simultaneously with XRD patterns of Fig. 8.

in raising C<sub>2</sub> yield, though the catalyst phase and CO<sub>2</sub> production appear to be unaffected.

To further test this, an experiment was carried out using Mn<sub>3</sub>O<sub>4</sub> as starting material in the presence of a KCl reservoir. After a short period in a KCl vapour, this arrangement should effectively simulate a KCl-promoted catalyst, and our own reactor studies have indeed demonstrated that such systems show essentially identical steady state performance to materials precalcined with KCl (11). Figure 10 shows that the solid phase is unchanged as Mn<sub>3</sub>O<sub>4</sub> throughout the experiment, both before and after CHCl<sub>3</sub> injection. Figure 11 demonstrates that *on CHCl<sub>3</sub> injection CO<sub>2</sub> production is left unchanged, but a major increase in steady state C<sub>2</sub> production is observed.* (Note that in this particular case the reaction was operated under conditions of incomplete oxygen consumption). This provides strong support for the idea that the rate of CO<sub>2</sub> production is dependent on the solid phase present (and the presence or absence of K-promotion); chlorine promotion via the gas phases is responsible only for an increase in C<sub>2</sub> yield ("ionic" KCl-derived chlorine appears unable to produce this effect). The pulse of

CHCl<sub>3</sub> can also be important in producing strongly reducing conditions which force the catalyst into its most stable and selective phase, Mn<sub>3</sub>O<sub>4</sub>; however, this latter effect derives from the combustion of the carbon and hydrogen and is not dependent on the presence of gaseous chlorocompounds.

How does the gas phase chlorine promotion achieve its effect? Does it modify or create active centres for methane activation on the catalyst surface? Or is chlorine merely retained on the surface and slowly released into the gas phase where it induces homogeneous chemistry? Experiments carried out by Burch *et al.* (4, 5) suggest that the concentrations of chlorine compounds in the gas phase over similar catalysts are insufficient to explain the increase in selectivity in terms of purely homogeneous reactions. Three lines of evidence from the present work support this result. First, the effect of gas phase chlorine promotion appears permanent, both on the timescale of the *in situ* XRD experiments reported here, and in reactor studies carried out for up to 48 h. Second, control experiments in which CHCl<sub>3</sub> was injected into the reaction cell in the absence of catalyst showed that the effect died away in under 1 h, despite the large area of ceramic, silica, and steel (thermocouple) available for chlorine to reside on before being evolved into the gas phase where it could induce homogeneous reactions. Note that the porous, gas-permeable ceramic on which the sample was mounted (Fig. 1) provided a large area hot surface on which such processes could occur. Thus the empty cell did have potential for generating long-lived homogeneous reactions, but these were not observed. Third, the different catalysts show very significant variation in the promotional effects due to gas phase chlorine (compare for example Figs. 2 and 6); this despite the fact that similar adsorption/desorption behaviour of chlorine from the surface might be expected in all cases, since Mn<sub>3</sub>O<sub>4</sub> is always the phase present.

Thus, although our results provide no *single* conclusive piece of evidence to support

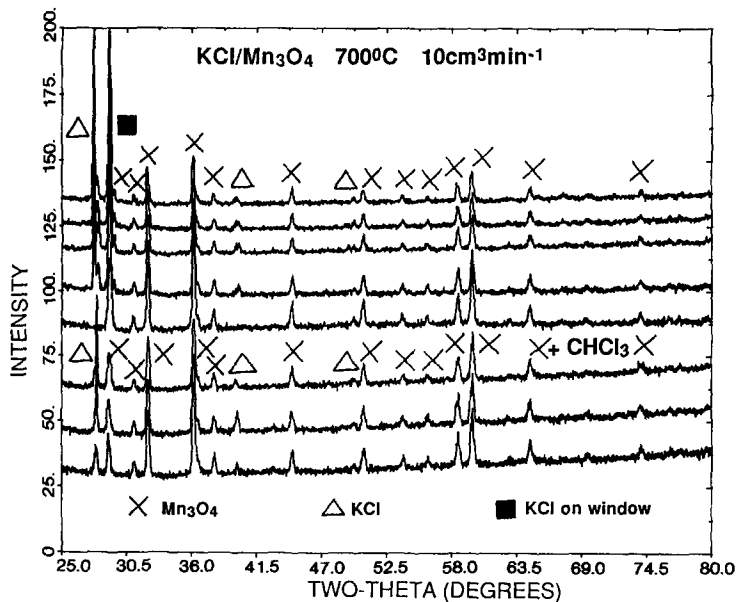


FIG. 10.  $\text{Mn}_3\text{O}_4$  + KCl reservoir,  $700^\circ\text{C}$ , gas flow rate  $10 \text{ cm}^3 \text{ min}^{-1}$ . XRD patterns recorded sequentially over 1 h each, starting 1 h after onset of heating.  $5 \mu\text{L}$   $\text{CHCl}_3$  injected after third scan.

the view that catalyst promotion by gaseous chlorocompounds is heterogeneous and not homogeneous in origin, there are several lines of evidence which do provide very strong support for this idea, which is also

corroborated by the work of Burch and co-workers (4, 6).

#### CONCLUSION

1. The only manganese oxide phase capable of good  $\text{C}_2$  selectivity is  $\text{Mn}_3\text{O}_4$ , in agreement with the work of Burch *et al.* (4–6). KCl-promoted  $\text{Mn}_3\text{O}_4$  is a good methane coupling catalyst. However, *unpromoted*  $\text{Mn}_3\text{O}_4$  itself is a good combustion catalyst, and is also rather prone to reduction to  $\text{MnO}$  under our reaction conditions.

2. The presence of a potassium promoter seems to ensure the stability of the  $\text{Mn}_3\text{O}_4$  phase as well as drastically reducing its  $\text{CO}_2$  formation activity and raising  $\text{C}_2$  activity. Other solid phases have much higher activities for the total oxidation of methane than does  $\text{Mn}_3\text{O}_4$ .

3. The role of potassium promotion is to raise  $\text{C}_2$  selectivity of the  $\text{Mn}_3\text{O}_4$  phase. This seems to be achieved by stabilising higher oxidation states of manganese. Such an effect is consistent with promotion by a redox mechanism; either by accelerating regenera-

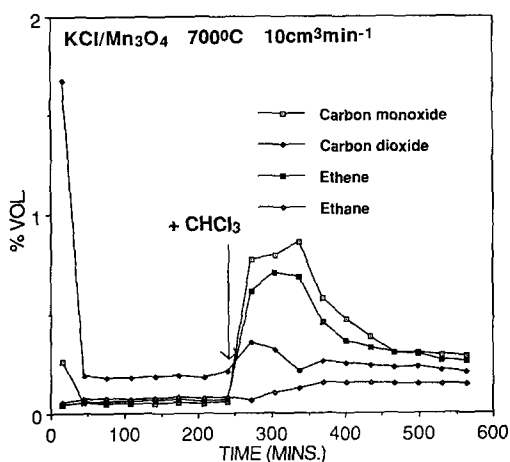


FIG. 11.  $\text{Mn}_3\text{O}_4$  + KCl reservoir,  $700^\circ\text{C}$  gas flow rate  $10 \text{ cm}^3 \text{ min}^{-1}$ . Reaction data acquired simultaneously with XRD patterns of Fig. 10.

tion of reduced sites, or by enhancing the availability of active, oxidised sites. Potassium may also act to enhance chlorine retention by the working catalyst.

4. The presence of chloride ions seems to be essential to prevent the formation of potassium manganese oxide phases, which are highly unselective. Ionic chlorine, however, is unable to produce the promotional effects of gas phase chlorine.

5. The introduction of chlorine via the gas phase raises the activity of  $Mn_3O_4$  for  $C_2$  formation, whilst leaving  $CO_2$  production unaffected. This form of promotion is enhanced by the presence of KCl; the duration of this form of promotion is also greatly increased by the presence of KCl. There are strong indications that such promotion occurs by site modification or by the formation of active chlorine radicals on the surface, rather than via purely homogeneous chemistry.

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