

The Oxidative Coupling of Methane on Mn/SiO₂ and the Effect of Solid- and Gas-Phase Doping

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The presence of a small quantity of tetrachloromethane in the reactant stream promotes the oxidative coupling of methane over silica-supported alkali-added manganese oxide catalysts. The choice of the alkali metal and of the anion employed to introduce the alkali metal to the catalyst was found to affect considerably the extent of TCM promotion. Mn/SiO₂ catalyst heavily doped with Na or K behaves as a promising catalyst for the coupling reaction in the presence of TCM, producing 20–22% yield of C₂ hydrocarbons with a selectivity of 75–80%. The formation of an active chlorine species on the surface of the solid is suggested to alter its catalytic properties, which generates a new route, in addition to that occurring in the absence of chlorine species, for the coupling of methane. © 1990 Academic Press, Inc.

INTRODUCTION

The search for suitable catalysts in the oxidative coupling of methane has included a wide variety of catalysts (1, 2). A number of oxides of metals such as those of Mn, Sn, Pb, Bi, Be, Mg, Ca, Sr, and Ba (3–13) have been tested. The addition of alkali compounds, usually in relatively small amounts, has frequently been shown to produce advantageous effects (5, 10–12). In particular, manganese oxide has been examined for methane conversion by a number of workers. The consequences of the addition of alkali metals to these catalysts (10, 11) have been studied and the importance of homogeneous reactions has been assessed by comparison of the results obtained in the absence of a catalyst and with LiCl/MnO₂ (14, 15).

The effect of the introduction of gas-phase additives in methane conversion processes has been studied in this laboratory (16–22). The addition of small quantities, usually less than 0.5 mol%, of tetrachloromethane to the feed stream in the conversion of methane on

heteropoly oxometalates produces substantial changes in conversions and selectivities. On 12-molybdophosphoric acid (16, 17, 19), an increased yield of formaldehyde was observed while with 12-tungstophosphoric acid (16, 18, 19), methyl chloride with selectivity up to 80% was produced with little or no change in the yield of formaldehyde.

Subsequently these studies have been extended to oxides with which substantial changes in both the conversions and selectivities to C₂ hydrocarbons have been observed (20–22). Preliminary work demonstrated that, at 775°C, the introduction of approximately 1 Torr of CCl₄ to the feed stream of methane and oxygen (63 and 60 Torr, respectively) enhanced the yield of C₂ hydrocarbons by a factor of approximately 5 with a silica-supported manganese oxide catalyst.

The present study is concerned with the examination of the effect of the introduction of tetrachloromethane into the methane conversion feed stream passing over a manganese oxide/SiO₂ catalyst doped with an alkali metal. A number of variables are considered including the nature of the alkali metal, the preparative anion, relative

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amounts of CH₄ and O₂, the residence time, and the onstream time.

EXPERIMENTAL

The supported catalysts were prepared by coimpregnating the silica (Grace-Davison, grade 407, 8–20 mesh, surface area of ~740 m² g) with a solution containing appropriate amounts of manganese nitrate and an alkali metal salt at 80–90°C with stirring. The samples were further dried in air at 110°C for 3 h and then calcined in air at 775°C for 4 h. The loading of the catalysts is expressed as weight percent metal against 100 wt% silica.

The catalytic experiments were conducted in a fixed-bed, flow-type reaction system under atmospheric pressure. The reactor was a quartz tube (9 mm i.d. × 35 mm) which was sealed on two ends with 4-mm-i.d. quartz tubing (the total length of the reactor was ~200 mm). The catalyst was placed in the 9-mm-i.d. portion of the reactor the length of which was just sufficient to accommodate the catalyst particles. In some experiments, when smaller amounts of catalyst were employed, 7- or 4-mm-i.d. tubes were used to pack the catalyst. The catalyst bed was held in place with two quartz wool plugs. The reactor was designed to keep the free volume at a minimum in the hottest zone of the reactor so as to minimize purely homogeneous conversion of methane. The carbon tetrachloride additive was introduced into the main flow of reactants (CH₄, O₂ and diluent He) by bubbling a separate flow of helium through the liquid. The vapor pressure of TCM was controlled by adjusting the temperature of the saturator and the flow of helium. In all experiments the catalyst, after being heated to 775°C under a flow of helium, was pretreated with a flow of oxygen (25 ml/min) for 1 h. Then the reactor was purged with helium. In general at this point a feed mixture consisting of CH₄, O₂, and He (no CCl₄) was introduced to the reactor. Preliminary experiments indicated that in the absence of TCM the deactivation of the catalyst with time on stream was negligible at least for the first few hours.

Therefore when TCM was absent the reaction was allowed to proceed for ~½ h prior to the analysis of reaction products, after which time TCM was included in the feed flow and the effluent was sampled periodically and analyzed. In the presence of TCM, with a number of the catalysts, the conversion and selectivities remained virtually constant with time on stream, while with others significant changes in these quantities were noted with time on stream. The results presented in this paper, unless otherwise stated, represent data collected at ~½ h of time on stream, which in most cases correspond to near steady-state values. Those catalysts which display significant changes in activity and selectivity with time on stream are subsequently specified in the text. The temperature referred to here was measured by placing a thermocouple in contact with the outside wall of the reactor immediately adjacent to the catalyst bed. The contact time of the feed on the catalyst bed was changed by varying the weight of the catalyst while holding the gas flow rate fixed.

The composition of the effluent gases was analyzed with an on-line HP 5890 gas chromatograph equipped with a thermal conductivity detector and attached to a HP 3392 integrator. The columns used for separation were Porapak T (18 ft. × ¼ in.), programmed 30–140°C, and Molecular Sieve 5A (1 m × ¼ in., 30°C) which were connected in series through a VALCO switching valve. O₂, CH₄, and CO eluted rapidly from the Porapak T column and were separated on the Molecular Sieve column. Following elution of these gases, the Molecular Sieve column was isolated by switching the valve position while CO₂, CH₄, C₂, and C₃ hydrocarbons, CH₃Cl, and H₂O were eluted from the Porapak T column.

The conversion and selectivities were calculated on the basis of the amount of reaction products formed as determined by the GC analysis. The amounts of methane and oxygen in the feed were determined from GC analysis in which the reactor was by-

passed. The conversion of methane ($x\text{CH}_4$) and selectivity to a product i (S_i) are defined as follows:

$$x\text{CH}_4 = \frac{100 \times \sum \text{moles of a product } i \times \text{no. of carbon atoms in the product } i}{\text{moles of CH}_4 \text{ present in the feed}}$$

$$S_i = 100 \times \frac{\text{moles of a product } i \times \text{no. of carbon atoms in the product } i}{\sum \text{moles of a product } i \times \text{no. of carbon atoms in the product } i}$$

The yield to a product is defined as conversion times selectivity.

Blank experiments conducted with CH_4 absent from the feed ($\text{O}_2 + \text{He} + \text{CCl}_4$) indicated that CCl_4 undergoes oxidation producing CO and CO_2 . However, the quantities of CO and CO_2 were negligibly small compared to those produced when CH_4 was present in the feed. Nevertheless, the data reported were corrected by running duplicate experiments with CH_4 absent under otherwise identical sets of process variables. The predominant chlorine-containing product Cl_2 .

RESULTS

Figure 1 shows the catalytic performance of Mn/SiO_2 catalysts with various alkali metals added in both the presence and the absence of TCM in the feed stream. Also included in the figures are the results obtained with undoped Mn/SiO_2 for purposes of comparison. Evidently over undoped Mn/SiO_2 the presence of TCM in the feed has a relatively small effect on the conversion and the total selectivity to C_2 hydrocarbons. The doped catalysts included in this figure were prepared from manganese nitrate and the respective alkali acetate. The quantities of salts used in the preparation were adjusted to give alkali metal/manganese ratios of 0.237 (atom/atom). It is evident from the figure that, on introduction of TCM to the feed, the conversion of CH_4 was markedly enhanced with the Li-, Na-, and

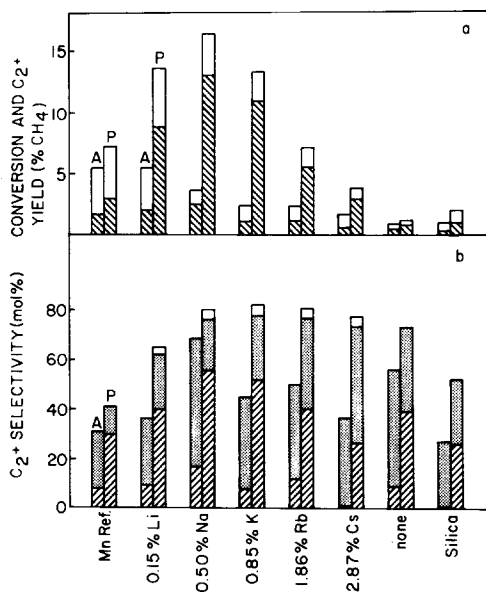


FIG. 1. The effect of cation of the dopant in alkali-doped manganese oxide (silica-supported) catalysts on oxidative coupling of methane. A and P represent TCM absent and present, respectively. Mn loading is 5.0 wt% and alkali loading is as indicated, which corresponds to alkali/Mn = 0.237 on an atomic basis. Alkali acetate was used to introduce alkali cation. The notation Mn Ref. represents Mn/SiO_2 with no addition of alkali. $W = 1.5$ g, $F = 30$ ml min^{-1} , $T = 775^\circ\text{C}$, $\text{CH}_4 = 215$ Torr, $\text{O}_2 = 28$ Torr, TCM = 0.35 Torr (when present). (a) \square , CH_4 conversion; ▨ , C_2^+ yield. (b) ▨ , C_2H_4 ; ▩ , C_2H_6 ; \square , $\text{C}_2\text{H}_2 + \text{C}_3$.

K-added Mn/SiO_2 catalysts to the extent that the oxygen conversion approached completion, while with the Rb- and Cs-added catalysts the effect was not as pronounced. In the absence of TCM, upon incorporation of alkali metal on the catalyst, the conversion declined gradually in the order $\text{Mn} \approx \text{Li-Mn} > \text{Na-Mn} > \text{K-Mn} > \text{Rb-Mn} > \text{Cs-Mn}$. In the presence of TCM, the conversion decreased in the order $\text{Li-Mn} \approx \text{Na-Mn} \sim \text{K-Mn} > \text{Mn} \approx \text{Rb-Mn} > \text{Cs-Mn}$ (note the limited supply of oxygen with the first three catalysts). The selectivity to C_2^+ hydrocarbons, in the absence of TCM, was highest with $\text{Na-Mn}/\text{SiO}_2$ catalysts ($\sim 70\%$), while with other alkali-added Mn/SiO_2 catalysts, the selectivity ranged from 35–50%. Upon introduction of TCM,

the selectivity to C₂⁺ hydrocarbons increased to 65% for the Li-added catalyst and to 80% for other alkali-metal-added catalysts. In the presence of TCM in the feed, the yield of C₂⁺ hydrocarbons increased from 2 to 9% with Li-Mn/SiO₂, from 2 to 13% on Na-Mn/SiO₂, and from 1 to 11% on K-Mn/SiO₂ while the corresponding increases in the selectivity were from 35 to 65%, from 70 to 80%, and from 50 to 80% on these catalysts, respectively. The presence of TCM also increases the proportion of C₂H₄ in the C₂ fraction of the products. It should be mentioned that in the absence of TCM the conversion and C₂⁺ selectivity changed very little with time on steam, while in the presence of TCM the conversion decreased significantly and the selectivity to C₂H₄ and to CO₂ considerably decreased and increased, respectively, with time on stream, particularly with Mn/SiO₂ catalysts where Li, Na, and K had been incorporated.

Figure 2 illustrates the effect of the dopant anion of the sodium-doped Mn/SiO₂ catalysts on the initial conversion and selectivity. In the absence of TCM, with NaCl as the precursor in the preparation of the Na-Mn/SiO₂ catalyst, the conversion was much higher than with NaNO₃ or NaCH₃COO. The yield of C₂⁺ hydrocarbons was also considerably higher with NaCl-doped catalyst but the C₂⁺ selectivity was somewhat lower. In the presence of TCM in the feed stream, on the other hand, the initial conversion, total C₂⁺ selectivity, and yield were comparable with the three catalysts. However, with time on stream, conversion, and C₂⁺ selectivity decreased and the change in the latter was considerably more pronounced with the NaCl-doped catalyst than with NaNO₃- and NaCH₃COO-doped catalysts. Evidently, with all three catalysts, the yield of C₂⁺ hydrocarbons increased considerably upon introduction of TCM into the feed, and the effect, on the relative scale, was more pronounced with the nitrate or acetate salt of sodium as the dopant in the preparation of the catalyst. In the remainder of this study the nitrate or acetate of the alkali cation has

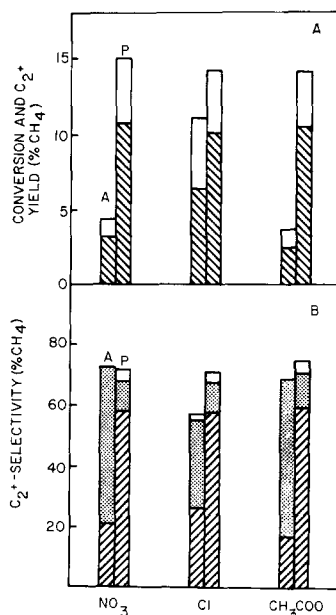


FIG. 2. The effect of anion of the dopant in sodium-doped manganese oxide (silica-supported) catalysts on conversion and selectivity. A and P indicate TCM absent and present, respectively. Catalyst composition: Mn = 5.0 wt%, Na = 0.50 wt%. $W = 1.5$ g, $F = 30$ ml/min, $T = 775^\circ\text{C}$, $\text{CH}_4 = 215$ Torr, $\text{O}_2 = 28$ Torr, TCM = 1.2 Torr. (A) \square , CH₄ conversion; \blacksquare , C₂⁺ yield. (B) ▨ , C₂H₄; ▩ , C₂H₆; \square , C₂H₂ + C₃.

been used in the preparation of the catalyst to illustrate the effect of gaseous TCM on the conversions.

Figure 3 shows the conversion of methane and the product selectivity as a function of Na content of mixed Na-Mn/SiO₂ catalysts. In the absence of TCM, with the addition of Na the conversion first drops slightly and then increases gradually and finally levels off to a constant value. In the presence of TCM in the feed, with the addition of Na, the conversion increases rapidly and then levels off to a constant value (oxygen conversion approaches completion). Evidently, with the Na-Mn/SiO₂ system the conversion achieved is considerably higher in the presence of TCM than in its absence. The selectivity to C₂⁺ hydrocarbons which, in both the presence and the absence of TCM, increases with increasing Na content of the

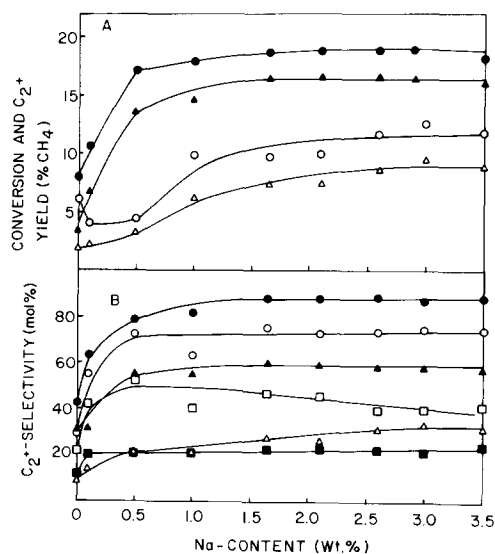


FIG. 3. The effect of TCM as a function of Na content in Na-Mn/SiO₂ catalysts on conversion, yield, and selectivity. Mn loading = 5.0 wt%. NaNO₃ was used to introduce sodium cation. $W = 1.5$ g, $F = 30$ ml/min, $T = 775^\circ\text{C}$, $\text{CH}_4 = 215$ Torr, $\text{O}_2 = 28$ Torr, TCM = 0.35 Torr. Open symbols, TCM absent; solid symbols, TCM present. (A) \circ , \bullet , CH₄ conversion; \triangle , \blacktriangle , C₂⁺ yield. (B) \triangle , \blacktriangle , C₂H₄; \square , \blacksquare , C₂H₆; \circ , \bullet , C₂⁺ total.

catalyst up to about 0.5 wt%, is about 10–15% higher in the presence of TCM. With increasing Na content of the catalyst, in the absence of TCM, the selectivity to C₂H₆ increased to a broad maximum and then slowly decreased while the selectivity to C₂H₄ slowly increased. In the presence of TCM, the selectivity to both C₂H₆ and C₂H₄ remained virtually constant after initial increases. Evidently, in the absence of TCM, the selectivity to C₂H₆ was considerably higher than that to C₂H₄, while in the presence of TCM, the selectivity to C₂H₄ was markedly higher than that to C₂H₆. In the absence of TCM the conversion and selectivities to different products changed only to a very small extent with time on stream. In the presence of TCM, on the other hand, with catalyst containing less than 2 wt% Na, the conversion of CH₄ and selectivity to C₂H₄ decreased significantly with time on stream and the selectivity to CO and to C₂H₆

remaining more or less constant and that to CO₂ increased, while with catalysts containing more than 2 wt% Na, conversion and selectivities to different products remained relatively unchanged with time on stream.

Table I illustrates the effect of the concentration of TCM in the feed. Evidently, the presence of small quantities of TCM in the feed dramatically increased conversion of methane and yield of C₂⁺ hydrocarbons. The presence of TCM did not however substantially influence total C₂⁺ selectivity, but did considerably affect the proportion of C₂H₄ in the C₂-fraction of the products. Table I also illustrates that the presence of TCM in the feed in amounts exceeding 0.35 Torr had somewhat deleterious effects on C₂⁺ selectivity and yield. It is evident that the qualitative nature of the results is independent of the anion of the sodium salts used in the preparation of the catalyst. In the remainder of this report TCM used in the feed was 0.35 Torr.

The effects of partial pressures of reactants on conversion and selectivities with Na-Mn/SiO₂ and K-Mn/SiO₂ catalysts are shown in Figs. 4 and 5, respectively. Over both catalysts, increasing pressure of oxygen under a definite pressure of methane, increases the conversion of methane consid-

TABLE I

Effect of Concentration of TCM in the Feed on Conversion and Selectivity on Na-Mn/SiO₂

TCM concentration (Torr)	CH ₄ conversion (%)	Selectivity (%)			C ₂ ⁺ yield (% CH ₄)
		C ₂ H ₆	C ₂ H ₄	C ₂ ⁺ total	
0 ^a	4.4	51.7	20.8	72.5	3.2
0.35 ^a	17.1	19.5	54.9	78.9	13.5
0.60 ^a	15.5	15.3	56.9	76.7	11.9
1.2 ^a	15.	9.8	57.9	71.5	10.7
0 ^b	3.7	51.7	16.7	68.4	2.5
0.35 ^b	16.3	20.3	55.6	80.8	13.2
1.2 ^b	14.1	11.3	59.3	74.6	10.5

Note. $W = 1.5$ g, $F = 30$ ml min⁻¹, $T = 775^\circ\text{C}$, $\text{CH}_4 = 215$ Torr, $\text{O}_2 = 28$ Torr.

^a Catalyst prepared from Mn-nitrate and Na-nitrate (Mn = 5.0 wt%, Na = 0.5 wt%).

^b Catalyst prepared from Mn-nitrate and Na-acetate (Mn = 5.0 wt%, Na = 0.5 wt%).

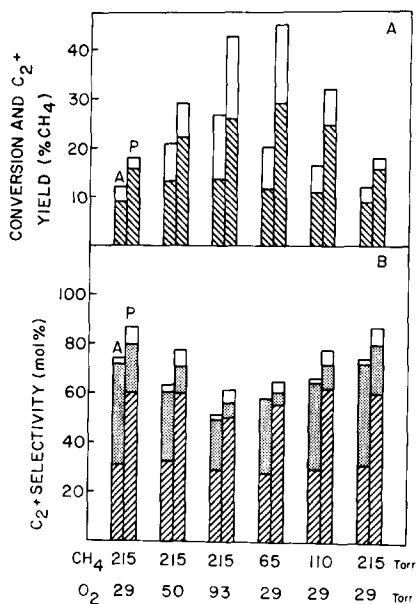


FIG. 4. Conversion and selectivities as a function of partial pressures of reactants on Na-Mn/SiO₂ (Na = 3.5 wt%, Mn = 5.0 wt%). NaNO₃ was used to introduce sodium. A and P indicate TCM absent and present, respectively. $W = 1.5$ g, $F = 30$ ml/min, $T = 775^\circ\text{C}$, TCM = 0.35 Torr (when present). (A) \square , CH₄ conversion; \square , C₂ + yield. (B) \square , C₂H₄; \square , C₂H₆; \square , C₂H₂ + C₃.

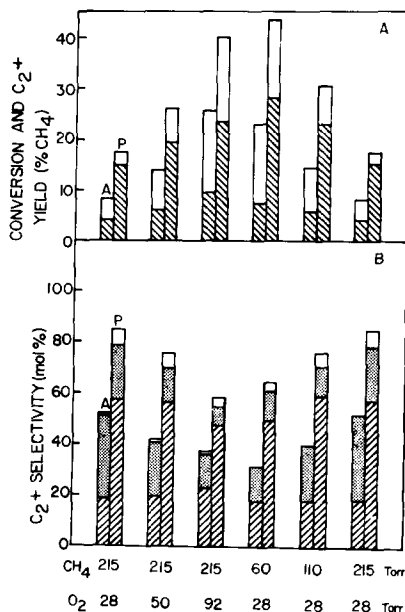


FIG. 5. Conversion and selectivities as a function of partial pressures of reactants on K-Mn/SiO₂ (K = 5.95 wt%, Mn = 5.0 wt%). KNO₃ was used to introduce potassium. A and P indicate TCM absent and present, respectively. $W = 1.5$ g, $F = 30$ ml/min, $T = 775^\circ\text{C}$, TCM = 0.35 Torr (when present). (A) \square , CH₄ conversion; \square , C₂⁺ yield. (B) \square , C₂H₄; \square , C₂H₆; \square , C₂H₂ + C₃.

erably in both the presence and the absence of TCM. The yield of C₂⁺ hydrocarbons also increased with increasing oxygen pressure but the effect is much less marked compared to that of conversion. Increasing the pressure of methane at a definite pressure of oxygen decreases the conversion in both the presence and the absence of TCM. The yield of C₂⁺ hydrocarbons also decreases with increasing methane pressure, but again the effect is less marked than that with conversion. Evidently, conversion of methane and, more importantly, C₂⁺ yield are considerably higher in the presence of TCM in the feed and, with Na-Mn/SiO₂ catalyst, the oxygen conversion reached nearly 100% under all sets of feed compositions employed. Figures 4b and 5b illustrate that in spite of a considerably higher yield of C₂⁺ hydrocarbons obtained in the presence of TCM, the

C₂⁺ selectivities achieved are comparable and, in fact, somewhat higher with TCM present. However, the proportions of C₂H₆ and C₂H₄ in the C₂-fraction of the products are markedly different in the absence and in the presence of TCM. In the absence of TCM, selectivities to C₂H₆ and C₂H₄ are similar, while in the presence of TCM, the selectivity to C₂H₄ is much higher than that to C₂H₆. Furthermore, the ratio C₂H₄/C₂H₆ in the products increases with increasing partial pressure of oxygen and decreases with increasing partial pressure of methane in the feed stream. In general, both with and without the presence of TCM, increases in the pressure of O₂ reduce selectivity to C₂⁺ products, while the selectivity increases with the pressure of CH₄.

The effect of contact time shown in Fig. 6 illustrates that, in the absence of TCM, the

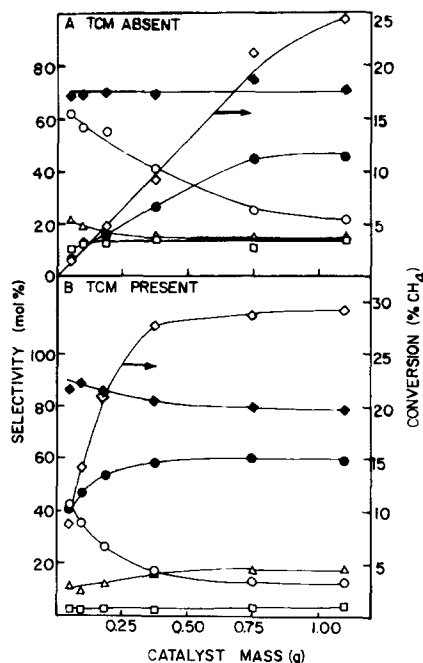


FIG. 6. The effect of contact time on conversion and selectivity in the absence and presence of TCM on Na-Mn/SiO₂ catalyst (Na = 3.0 wt%, Mn = 5.0 wt%). NaNO₃ was used to introduce sodium. $F = 30$ ml/min, $T = 775^{\circ}\text{C}$, $\text{CH}_4 = 215$ Torr, $\text{O}_2 = 52$ Torr, TCM = 0.35 Torr. \diamond , CH₄ conversion; \triangle , CO; \square , CO₂; \circ , C₂H₆; \bullet , C₂H₄; \blacklozenge , C₂ + total.

conversion increases linearly with contact time at lower values of contact time, suggesting that the conversion process is predominantly catalytic and that diffusional effects are absent. At the highest value of contact time employed, deviation from linearity was due to a limited supply of oxygen in the feed. In the presence of TCM, deviation from linearity due to this limited availability of oxygen was evident at even shorter contact time. However, it appears that the conversion (with TCM) does not exhibit a linear relationship with contact time even at very short residence time and this may suggest that a heterogeneous-homogeneous mechanism is operating in the presence of TCM. The total selectivity to C₂⁺ hydrocarbons remained independent of contact time in the absence of TCM suggesting that secondary oxidation of product hydrocarbons

is insignificant. However, in the presence of TCM, C₂⁺ selectivity declined slightly with time of contact, suggesting that CO_x, apart from being produced directly from methane, may have also been generated to some extent from product hydrocarbons. It should be recalled, however, that in this set of experiments the contact time of the reactants and products with the catalyst surface was varied by changing the mass of the catalyst while maintaining the gaseous flow fixed. At the same time, the diameter of the reactor in that section containing the catalyst particles was adjusted so that the void space in the hottest zone of the reactor was reduced to a minimum. As a result, as the catalyst mass used in the experiment was reduced, the contact time of the species present on the catalyst decreased accordingly, but the variation in the residence time of the species present in the free volume of the reactor is somewhat uncertain. However, in view of the aforementioned variation in the reactor size, the assumption that the latter parameter was unchanged or slightly decreased appears to be valid. Therefore, while the heterogeneous contribution to the secondary oxidation of C₂ hydrocarbons appears to be relatively small with the catalysts of the present study, the possibility of the occurrence of such reactions to a significant extent in the gas phase cannot be dismissed. In both the absence and the presence of TCM, selectivity to C₂H₆ and to C₂H₄ decreases and increases, respectively, with time of contact, suggesting that C₂H₄ is at least partly a secondary product to C₂H₆. The selectivities to CO and CO₂ show a very weak dependence on contact time, suggesting that heterogeneous oxidation of CO to CO₂ is relatively slow with the catalysts employed in the present work.

Figure 7 illustrates that with a 3.5 wt% Na-5 wt% Mn/SiO₂ catalyst, when TCM was continuously introduced into the feed, yields of both C₂⁺ hydrocarbons and CO_x (hence respective selectivities to total conversion) remained constant with time on stream. However, when the catalyst was

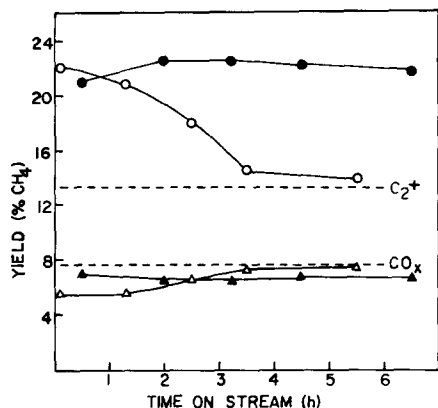


FIG. 7. The effect of short pretreatment vs continuous treatment of the catalyst with TCM on the yields of different products on Na-Mn/SiO₂ (Na = 3.5 wt%, Mn = 5.0 wt%). NaNO₃ was used to introduce Na. *W* = 1.5 g, *T* = 775°C, *F* = 30 ml/min, CH₄ = 215 Torr, O₂ ~ 50 Torr, TCM = 0.35 Torr. Solid symbols: No pretreatment; feed: CH₄ + O₂ + TCM + He. Open symbols: Pretreated with TCM + O₂ He (1½ h); feed: CH₄ + O₂ + He. Broken lines: No pretreatment; feed: CH₄ + O₂ + He. ○●, C₂⁺; △▲, CO_x.

pretreated with a flow of He + O₂ + TCM mixture and then exposed to a flow of CH₄ + O₂ + He but with TCM absent (after thoroughly purging the system to eliminate TCM from the gas phase), initially high yields of C₂⁺ hydrocarbons, compared to that when TCM was continuously fed, were produced, but the yield gradually dropped and after a few hours of time on stream approached that which was obtained when the catalyst had not been exposed to TCM (Fig. 7).

In Table 2 results obtained with Li-Mn/SiO₂-based catalysts are presented. Evidently, with catalysts prepared from lithium nitrate (or acetate) and manganese nitrate, the presence of TCM in the feed increased the selectivity and yield of C₂⁺ hydrocarbons although the effect was not as pronounced as that with Na-Mn/SiO₂ catalysts. The presence of TCM also increases the ratio of C₂H₄/C₂H₆ in the products. However, when lithium chloride was used as the impregnating agent in the preparation of the catalyst, the presence of TCM only increased the ra-

tio C₂H₄/C₂H₆ in the products but did not significantly affect the total selectivity or yield of C₂⁺ hydrocarbons. Furthermore, when lithium nitrate was the impregnating salt in the preparation of catalysts and reactions were performed in the presence of TCM, the conversion and selectivities remained unchanged with time on stream, while when lithium chloride was the impregnating material conversion of methane and selectivity to C₂⁺ hydrocarbons (more specifically, to C₂H₄) decreased rapidly with time on stream.

Some experiments were also performed to test the fate of C₂H₆ when passed through the reactor with or without the presence of catalyst, in both the presence and the absence of TCM (Table 3).

DISCUSSION

This paper demonstrates the beneficial effect of introducing TCM to the feed in the oxidative coupling of methane on silica-supported alkali-added manganese-based catalysts. Evidently, Li-, Na-, and K-doped catalysts, in particular the latter two, showed maximum response to the presence of TCM in promoting the coupling process. With these catalysts the presence of TCM, in addition to considerably improving the selectivity to C₂ hydrocarbons, markedly increased the conversion of methane. With Na-Mn/SiO₂ and K-Mn/SiO₂, yields of 22.5% (selectivity = 78%) and 20% (selectivity = 75%) of C₂⁺ hydrocarbons, respectively, were obtained (Figs. 4 and 5).

In the case of the Na-Mn/SiO₂ catalyst, which was examined in some detail, the anion of the salt used to introduce the alkali metal to the catalyst seems to exert a considerable effect on the conversion and yield of C₂⁺ hydrocarbons in both the presence and the absence of TCM. In the absence of TCM the yield of C₂ hydrocarbons was considerably higher when NaCl was used in the preparation of the catalyst compared to that prepared from NaNO₃ or NaCH₃COO, although the C₂-selectivity was somewhat lower with the former catalyst. In the case

TABLE 2
Conversion and Selectivity on Li-Mn/SiO₂ Catalyst

Catalyst composition (wt%)			Conversion (%)		Selectivity				
Mn	Li		CH ₄	I ₂	CO	CO ₂	C ₂ H ₆	C ₂ H ₄	C ₂ ⁺ total
5	0.15 ^a	A	5.5	60	21.9	41.5	27.2	9.4	36.6
		P	13.6 (9.0)	95 (95)	16.4 (13.5)	18.7 (44.1)	21.8 (20.6)	40.3 (21.8)	64.9 (42.4)
5	0.50 ^b	A	8.7	100	22.3	47.3	21.6	8.7	30.13
		P	12.7 (12.6)	100 (100)	25.2 (27.0)	24.3 (22.3)	15.3 (13.8)	35.2 (36.9)	51 (50)
5	1.05 ^a	A	4.9		17.3	42.8	14.8	25.1	39.9
		P	12.7 (12.8)		19.3 (24.5)	24.1 (21.5)	21.8 (17.7)	32.7 (34.1)	(56.5) (53.3)
5	0.50 ^c	A	12.5	100	16.2	21.6	32.0	28.1	60.1
		P	12.2 (8.9)	100 (100)	19.9 (30)	22.9 (38.9)	12.4 (10.1)	41.9 (22.0)	(56)

Note. $W = 1.5$ g, $F = 30$ ml/min⁻¹, CH₄ = 215 Torr, O₂ = 28 Torr, TCM = 1.2 Torr (when present). Values in brackets for catalysts 1, 3, and 4 refer to results obtained after 5 h on stream while for catalyst 2 the values were obtained after 2.5 h on stream.

^a Catalyst prepared from Mn-nitrate and Li-acetate.

^b Catalyst prepared from Mn-nitrate and Li-nitrate.

^c Catalyst prepared from Mn-nitrate and LiCl.

TABLE 3
Homogeneous Conversion of Ethane

Feed	Catalyst ^a	Temp. (°C)	Conversion (%)		Selectivity (mol%)		C ₂ H ₄ yield (%)
			C ₂ H ₆	O ₂	C ₁ ^b	C ₂ H ₄	
C ₂ H ₆ + He	None	700	4.1	—	0.8	99.2	4.1
C ₂ H ₆ + He + O ₂	None	700	44	65	19.5	78.2	34.4
C ₂ H ₆ + He + TCM	None	700	10.7	—	3.2	96.8	10.4
C ₂ H ₆ + He + O ₂ + TCM	None	700	61	85	26.5	72.8	44.4
C ₂ H ₆ + He	None	775	36	—	2.0	97.5	35.1
C ₂ H ₆ + He + O ₂	None	775	75	90	27.2	70.8	53.1
C ₂ H ₆ + He + TCM	None	775	38.5	—	2.5	97.5	37.5
C ₂ H ₆ + He + O ₂ + TCM	None	775	87.5	~100	27.3	69.2	60.6
C ₂ H ₆ + He + O ₂	NaMn/SiO ₂	700	38.2	65	19.3	78.6	
C ₂ H ₆ + He + O ₂ + TCM	NaMn/SiO ₂	700	59	85	19.8	77.3	
C ₂ H ₆ + He + O ₂	NaMn/SiO ₂	775	73	~95	27.1	70.3	
C ₂ H ₆ + He + O ₂ + TCM	NaMn/SiO ₂	775	81	~96	28.7	69.3	

Note. $F = 30$ ml/min, C₂H₆ = 57 Torr, O₂ = 27 Torr (when present), TCM = 1.2 Torr.

^a None represents an empty reactor packed with quartz wool. The loading of Na-Mn/SiO₂ catalyst was 5.0 wt% Mn and 3.5 wt% Na. The mass of the catalyst used was 0.20 g.

^b C₁ includes CH₄, CO, and CO₂.

of Li-Mn/SiO₂ catalysts (Table 2), both selectivity and yield of C₂ hydrocarbons were considerably higher with the LiCl-Mn-based catalyst than with the LiNO₃-Mn-based catalyst when experiments were conducted in the absence of TCM. On the other hand, when the experiments were conducted in the presence of TCM, marked enhancements in the yields of C₂ hydrocarbons were observed with NaNO₃- and NaCH₃COO-modified Mn/SiO₂ catalyst but not with NaCl-modified Mn/SiO₂ catalyst. The presence of TCM did not however significantly influence C₂-selectivity with these catalysts, although the ratio C₂H₄/C₂H₆ in the products was considerably modified. With Li-Mn/SiO₂ catalysts, the presence of TCM considerably enhanced both yield and selectivity of C₂ hydrocarbons when the catalyst was prepared with LiNO₃ as the additive, but not when prepared with LiCl as the additive. Furthermore, with both Li-Mn/SiO₂ and Na-Mn/SiO₂ systems, when the reactions were conducted with TCM present, the samples prepared with LiCl and NaCl as solid additive rapidly lost their ability to generate C₂-hydrocarbons (both yield and selectivity declined) with time on stream, in contrast with the catalyst prepared with LiNO₃, NaNO₃, or NaCH₃COO as the additive, where the deactivation was considerably less significant. These results, together with those of pretreatment experiments, which indicated incorporation of chlorine in some form in the catalyst during exposure to TCM, suggest that, while the presence of small amounts of chlorine (in a form unknown at present) on the catalyst surface (as in the cases of NaNO₃-, NaCH₃COO-, or LiNO₃-added Mn/SiO₂ catalysts when experiments were performed in the presence of TCM in the gas phase or as in the case of NaCl- and LiCl-added Mn/SiO₂ when experiments were conducted in the absence of gas-phase TCM) has advantageous effects in the oxidative coupling of methane, the presence of excessive quantities of chlorine on the surface (as in the case of LiCl- or NaCl-added Mn/SiO₂ under

conditions of continuous exposure to TCM) has detrimental effects. These conclusions are further supported by the fact that with Na-Mn/SiO₂ catalyst made from NaNO₃ or NaCH₃COO (Table 1), use of higher concentrations of TCM in the feed reduced the yield of C₂⁺ hydrocarbons.

It is frequently proposed that the rate-controlling step in the methane conversion process is the activation of a methane molecule via abstraction of a hydrogen atom. In the present study it is noted that NaCl-modified Mn/SiO₂ catalyst is considerably more active in the methane conversion process than those modified with NaNO₃ or NaCH₃COO when the experiments are conducted in the absence of gas-phase TCM. However, the latter catalysts become markedly active in the production of C₂ hydrocarbons when small quantities of TCM are present in the gas phase. It is therefore tempting to argue that the chlorine species, whether it is introduced to the catalyst in advance during the preparation from solutions (as was done using NaCl or LiCl) or is generated *in situ* during the catalytic reaction by continuously cofeeding a chlorine-containing compound into the gaseous feed, facilitates the methane activation step, thereby producing considerable enhancement in the conversion of methane. It appears that the addition of TCM produces increases in the yield of C₂ hydrocarbons without affecting the yield of CO_x products significantly. Therefore it is plausible that the presence of TCM induces an activation process parallel to that taking place in the absence of TCM and this new process selectively promotes the coupling reaction. In this respect the phenomenon observed here differs from that reported by Burch *et al.* (14) involving unsupported Li- and Na-doped MnO₂ catalysts and by Fujimoto *et al.* (23) involving supported alkaline earth metal halide catalysts regarding chlorine promotion. Both studies suggested that the chlorine promotion results primarily from the inhibition of deep oxidation products. It may be noted that hydrocarbons have been shown to be

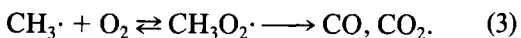
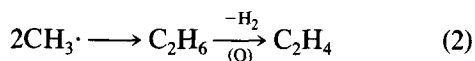
formed from methane and chlorine through the production of chlorinated methane which is subsequently pyrolyzed to yield C_2^+ hydrocarbons (24). Although there is some similarity of the present process to the latter process, the fact that the present reaction temperatures are much lower than those of the latter process and that the various alkali metal-incorporated manganese oxide-supported catalysts responded differently to the presence of TCM suggests that the present process cannot be purely homogeneous in nature. Further evidence for this is provided by the results of experiments involving passage of reactant mixtures with TCM present through an empty reactor (Fig. 1). Clearly, the magnitude of enhancement in the conversion process in the absence of a catalyst is negligible. It may therefore be inferred that the addition of TCM has caused changes in the character of the catalyst surface, presumably by forming an active chlorine species.

The effect of contact time on selectivities shows that in the absence of TCM, C_2 -hydrocarbon selectivity is virtually independent of the contact time of the species on the catalyst, while in the presence of TCM a slight drop in the C_2 -selectivity occurs at longer contact times. Nevertheless, considering the range of contact times employed (Fig. 6), it is reasonable to suggest that in both the presence and the absence of TCM, the secondary oxidation of C_2H_4 and C_2H_6 into nonselective oxygenated products on the catalysts employed is relatively insignificant, at least with the low ratio of O_2/CH_4 used in the set of experiments described in Fig. 6. The decrease in C_2H_6 selectivity and the increase in C_2H_4 selectivity with increasing time of contact suggest that C_2H_4 is at least partly produced from C_2H_6 . However, whether the process is heterogeneous or homogeneous or a combination of these is difficult to distinguish from this study. In any event, under most of the conditions of the present study C_2H_4 was the major product in the C_2 fraction of the products when TCM was present. Experiments in which ethane

was passed through an empty reactor packed with quartz wool showed that ethane undergoes substantial homogeneous dehydrogenation producing ethylene at $775^\circ C$. The addition of oxygen to the feed stream further enhanced this dehydrogenation process. At $700^\circ C$ in the presence of oxygen in the feed substantial dehydrogenation occurs as well, while in its absence conversion of C_2H_6 was quite small. Evidently, at $700^\circ C$ the dehydrogenation process becomes even more pronounced when TCM is introduced into the reactant stream, when O_2 was both absent from and present in the feed, while the effect was of lesser significance at $775^\circ C$. These results are summarized in Table 3. The table also illustrates that the introduction of the Na-Mn/SiO₂ catalyst did not substantially influence this dehydrogenation process regardless of the presence of TCM in the gas phase. These results suggest that under the conditions employed in this work rapid homogeneous dehydrogenation of the product C_2H_6 , both thermal and oxidative, is quite possible and a high ratio of C_2H_4/C_2H_6 in the product stream is therefore not surprising. Recently Burch *et al.* (14) also reported similar results for C_2H_6 dehydrogenation and arrived at similar conclusions. It may be noted however that in the present study the presence of TCM in the feed stream further enhanced the ratio C_2H_4/C_2H_6 in the products. Therefore under actual catalytic conditions the role of active chlorine species generated from TCM in affecting the ratio C_2H_4/C_2H_6 cannot be dismissed. Further support for this is provided from the observation that, in the absence of any catalyst, the ratio C_2H_4/C_2H_6 in the C_2 -fraction is also much higher when the conversion of CH_4 took place in the presence of TCM (Fig. 1). Weissman and Benson (25) have shown that at high temperatures chlorine radicals catalyze the formation of C_2H_4 from CH_4 in the gas phase. The participation of chlorine was also suggested by Otsuka and co-workers (26) and by Anshits *et al.* (27) to account for the high ratios of C_2H_4/C_2H_6 observed in the oxidative dimerization

of methane on LiCl-added NiO and MnO₂ catalysts and on CaCl₂-modified CaO catalysts, respectively. Thus it is possible that, under the conditions of the present study, C₂H₆ is the primary product of the coupling of methyl radicals, as has been concluded from other studies, but undergoes rapid thermal and oxidative dehydrogenation to C₂H₄, a process which is evidently further enhanced by the presence of TCM in the feed.

Many authors (2) have suggested that the oxidative coupling of methane proceeds with the abstraction of a hydrogen atom from a methane molecule, resulting in the formation of an OH species and a methyl radical on the solid surface. Methyl radicals then emanate into the gas phase and either undergo coupling reactions forming ethane or react with molecular oxygen, which results in the formation of carbon oxides. Ethylene is formed from the oxidative dehydrogenation of ethane.



The decline in C₂ selectivity with increasing partial pressure of oxygen or with increasing O₂/CH₄ ratio in the feed, as observed in both the presence and the absence of TCM in this study, can be interpreted as due to the displacement of the equilibrium (3) to increase the concentration of methylperoxy radicals, a precursor to carbon oxides. Although some support for the hypothesis that the above reactions involving radicals occur in the gas phase is provided by the observation of gaseous methyl radicals in the downstream from the reactor (2), the possible occurrence of these reactions, at least in part, on the catalyst surface cannot be entirely dismissed. Furthermore, reaction (3) may not be the major path for the production of nonselective oxygenated products. Methyl

radicals may also react with mono-oxygen species such as O⁻ and O²⁻ (lattice oxygen).

It appears from the present study that TCM, by forming an active chlorine species, alters the catalyst characteristics in a manner which promotes the yield and selectivity to C₂-hydrocarbons, in particular selectivity to ethylene on alkali-doped manganese catalysts supported on silica, but the nature of this active chlorine species is not yet understood. Furthermore, it appears that the presence of an alkali metal in the Mn/SiO₂ catalyst, but not again any alkali metal, is essential to observe the promoting effects. It is also not clear whether the promotion is a totally heterogeneous or a surface-mediated homogeneous phenomenon. Further studies are desirable to understand the fundamental aspects of chlorine promotion in the oxidative coupling process.

CONCLUSIONS

The following conclusions can be drawn from this study of the oxidation of methane on manganese-based catalysts: (1) Li-, Na-, and K-doped Mn/SiO₂ catalysts show considerable activity and selectivity in the coupling process. (2) This activity and selectivity, in particular the former, is markedly enhanced by cofeeding a small quantity of TCM in the feed stream. (3) The presence of TCM also facilitated the dehydrogenation of product ethane, thereby notably improving the selectivity to ethylene. (4) TCM establishes an additional route for the coupling reaction, presumably by creating new active sites or by modifying existing sites on the catalyst surface. (5) The secondary oxidation of C₂-hydrocarbons to complete oxidation products is of relatively minor importance with the catalysts and reaction conditions of this study.

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REFERENCES

1. Lee, J. S., and Oyama, S. T., *Catal. Rev. Sci. Eng.* **30**, 249 (1988).

2. Anderson, J. R., *Appl. Catal.* **47**, 177 (1989).
3. Keller, G. E., and Bhasin, M. M., *J. Catal.* **73**, 9 (1982).
4. Hinsen, W., and Baerns, M., *Chem. Ztg.* **107**, 223 (1983).
5. Hinsen, W., Bytyn, W., and Baerns, M., in "Proceedings, 8th International Congress on Catalysis, Berlin, 1984." Dechema, Frankfurt-au-Main, 1984.
6. Otsuka, K., Liu, Q., Hatano, M., and Morikawa, A., *Chem. Lett.*, 467 (1986).
7. Otsuka, K., Liu, Q., Hatano, M., and Morikawa, A., *Chem. Lett.*, 903 (1986).
8. Otsuka, K., and Komatsu, T., *Chem. Lett.*, 1955 (1986).
9. Sofranko, J. A., Leonard, J. J., and Jones, C. A., *J. Catal.* **103**, 302 (1987).
10. Jones, C. A., Leonard, J. J., and Sofranko, J. A., *J. Catal.* **103**, 311 (1987).
11. Sofranko, J. A., Leonard, J. J., Jones, C. A., Gaffney, A. M., and Withers, H. P., *Catal. Today* **3**, 127 (1988).
12. Matkuhashi, H., Sakurai, K., and Arata, K., *Chem. Lett.*, 585 (1989).
13. Carreiro, J. A. S. P., and Baerns, M., *J. Catal.* **117**, 258 (1989).
14. Burch, R., Squire, G. D., and Tsang, S. C., *Appl. Catal.* **46**, 69 (1989).
15. Burch, R., Crabb, E. M., Squire, G. D., and Tsang, S. C., *Catal. Lett.* **2**, 249 (1989).
16. Ahmed, S., and Moffat, J. B., *Catal. Lett.* **1**, 141 (1988).
17. Ahmed, S., and Moffat, J. B., *J. Phys. Chem.* **93**, 2542 (1989).
18. Ahmed, S., and Moffat, J. B., *J. Catal.* **118**, 281 (1989).
19. Ahmed, S., Kasztelan, S., and Moffat, J. B., *Discuss. Faraday Soc.*, **87**, 23 (1989).
20. Ahmed, S., and Moffat, J. B., *Catal. Lett.* **2**, 309 (1989).
21. Ahmed, S., and Moffat, J. B., *J. Catal.* **121**, 408 (1990).
22. Ahmed, S., and Moffat, J. B., *Appl. Catal.*, **58**, 83 (1990).
23. Fujimoto, K., Hashimoto, S., Arami, K., Omata, K., and Tominaga, H., *Appl. Catal.* **50**, 223 (1989).
24. Benson, S. W., U.S. Patent 4,199,533 (1980).
25. Weissman, M., and Benson, S. W., *Int. J. Chem. Kinet.* **16**, 307 (1984).
26. Otsuka, K., Hatano, M., and Komatsu, T., *Catal. Today* **4**, 409 (1989).
27. Anshits, A. G., Kirik, N. P., Roguleva, V. G., Shigapov, A. N., and Selyutin, G. E., *Catal. Today* **4**, 399 (1989).