

Promotion by Tetrachloromethane of the Oxidative Coupling of Methane on Silica-Supported Alkaline Earth Oxides

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Received March 6, 1989; revised September 7, 1989

The introduction of a small quantity of tetrachloromethane into the feed stream has been shown to remarkably enhance the oxidative coupling of methane over alkaline earth oxides supported on silica. That this enhancement, in terms of both selectivity and yield to C₂ hydrocarbons, occurs over a wide range of catalyst loading, feed composition, reaction temperature, and contact time has been illustrated using BaO/SiO₂ as the catalyst. It has been demonstrated that over this catalyst, the coupling and the nonselective oxidation processes occur predominantly independently of each other. The high ratio of C₂H₄/C₂H₆ observed in the products is accounted for by the rapid homogeneous oxidative dehydrogenation of C₂H₆, a process which is evidently further enhanced by the presence of TCM. It is suggested that TCM promotes the coupling reaction by facilitating the hydrogen abstraction step from methane. Continuous cofeeding of the additive is required to maintain high selectivity and yield of C₂ hydrocarbons in the products. © 1990 Academic Press, Inc.

INTRODUCTION

The catalytic conversion of methane by oxidative dehydrogenation to form ethane and ethylene has attracted considerable attention (1). The catalysts which have been proved to yield appreciable conversion and good selectivity include a number of pure and alkali-doped rare earth oxides (2, 3) and transition and main group oxides (4–12), as well as some complex oxides with rock salt structure (13) and layered oxychlorides (14). Although there have been fewer studies of the oxidative coupling of methane on supported catalysts, of those examined lead oxide supported on Al₂O₃ and MgO produce acceptable conversion and C₂ selectivity (15–17).

Both gas- and solid-phase additives have been examined for the methane conversion process although much less attention has been given to the former than to the latter. While the advantageous effects of the presence of a chlorine-containing compound in the feed stream in many catalytic processes

such as partial oxidation of ethylene (18) and hydrocarbon reforming processes (19) are well known, relatively little work has been reported on the effects of these additives in the methane conversion processes. Earlier studies have shown that, in the oxidation of methane, introduction of a halo-methane improves selectivity to formaldehyde on supported palladium and platinum catalysts (20, 21), while the introduction of chlorine improves selectivity to methanol on supported chromia catalysts (22, 23). More recently, the presence of gaseous HCl in the feed stream has been reported to promote coupling of methane to higher hydrocarbons on NaCl–MnO₂/SiO₂ catalyst (24). It is generally believed that in the case of alkali metal-doped oxides, the observed promoting actions in the formation of C₂ products from methane are due to the cations of the dopant. However, it is interesting to note that the highest selectivity to C₂ hydrocarbons was achieved when the corresponding chloride salts were used to introduce alkali metals in the catalyst (7, 10, 24–26).

In our recent studies (27–29) on the ap-

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plicability of silica-supported heteropoly oxometalates in the partial oxidation of methane with N_2O as oxidant, it was demonstrated that the introduction of a small quantity of dichloromethane (DCM) or tetrachloromethane (TCM) in the feed stream markedly increases the yield of H_2CO with 12-molybdophosphoric acid while on 12-tungstophosphoric acid monochloromethane is produced with a high selectivity. With both catalysts substantial increases in the conversion of methane occurred. In the light of these beneficial effects observed in the methane conversion over heteropoly oxometalates we have undertaken an extensive study on the effects of these chloroadditives in the oxidative coupling process using a variety of catalysts. In the present paper a detailed study of the effect of the presence of tetrachloromethane in the oxidative coupling of methane over alkaline earth oxide supported on silica, in particular on barium oxide, is presented. The effect of a number of variables such as loading, contact time, feed composition, and temperature on conversion and selectivity, both in the absence and presence of TCM, is examined. After completion of the present work, a report on the effect of pulsing dichloromethane and chloroform on samarium, magnesium and manganese oxide catalysts in the conversion of methane has appeared (30).

EXPERIMENTAL

The catalysts used were prepared by impregnating the support (Grace-Davison, grade 407, surface area of $\sim 740 \text{ m}^2 \text{ g}^{-1}$) with aqueous solutions of acetates at 80–90°C, followed by drying in air at 110°C for 3 h. The catalysts were finally calcined in air at 750°C for 4 h before charging to the reactor. The loading of the catalysts is expressed as weight percent metal against 100 wt% SiO_2 .

The catalytic experiments were performed in a fixed-bed continuous flow reactor operated under atmospheric pressure. The reactor consisted of an 8-mm-i.d. and

35-mm-long quartz tube sealed to 4-mm-i.d. quartz tubes on two ends (total length of the reactor was 200 mm). The catalyst was placed in the 8-mm-i.d. portion of the reactor whose length was just sufficient to accommodate the catalyst particles. In some cases, when smaller or larger amounts of catalyst were employed, 7 or 11-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 with the aim of minimizing the contribution of noncatalytic homogeneous reaction as far as possible. The additive, CCl_4 , was admitted to the main flow of reactants (CH_4 , O_2 , and diluent He) by passing a separate stream of helium through a gas dispersion tube in a glass saturator containing the liquid at ice-water temperature. In all experiments, the temperature of the catalyst was raised to 775°C while maintaining a continuous flow of helium and was then conditioned at this temperature under a flow of molecular oxygen ($F = 25 \text{ ml min}^{-1}$) for 1 h. The temperature of the reactor was then adjusted to reaction temperature (675–825°C) before the introduction of the reactant gas mixture consisting of methane, oxygen, and helium (total flow rate was 30 ml min^{-1} ; helium provided balance to the atmospheric pressure). The contact time of the catalyst was changed by varying the mass of the catalyst while the flow rate was held constant.

The reactants and products were analyzed on a HP 5890 gas chromatograph equipped with a TC detector and attached to an integrator. Porapak T (18 ft. $\times \frac{1}{8}$ in., programmed 30–140°C) was used to analyze CO_2 , C_2H_4 , C_2H_6 , C_3 hydrocarbons, H_2CO , H_2O , CH_3OH , and CH_3Cl . Molecular sieve 5A (1 m $\times \frac{1}{8}$ in., 30°C) was employed in the analysis of O_2 , N_2 , CO , and CH_4 . The columns were connected in series through a six-port VALCO switching valve to isolate the MS-5A column while CO_2 , the hydrocarbons, and H_2O are eluted from the Porapak T column. The conversion of

methane was calculated on the basis of products generated and methane introduced in the feed. The selectivities were calculated on the basis of the conversion of methane (expressed as mole percent) to each product. For example, the selectivity to ethylene was calculated as $100 \times (2 \times \text{moles of ethylene produced per mole of methane converted})$.

Experiments conducted in the absence of CH_4 in the feed showed that the chloroadditive, CCl_4 , undergoes oxidation to produce CO and CO_2 . Total quantities of $\text{CO} + \text{CO}_2$ produced from TCM in these experiments, were, however, in most cases insignificant compared to quantities of $\text{CO} + \text{CO}_2$ produced when CH_4 was present in the feed. In any event, data were corrected for the contribution from TCM by performing duplicate runs in the absence of CH_4 , under otherwise identical conditions of O_2 and TCM concentrations and residence times. The predominant chlorine-containing product was Cl_2 .

RESULTS

The major products of methane conversion were CO , CO_2 , C_2H_4 , and C_2H_6 . In the presence of TCM, in some experiments, measurable quantities of CH_3Cl and C_3 hydrocarbons were also produced, but, the latter accounted for less than 1% in the product distributions and were neglected in the calculations. In some experiments, such as those conducted in the absence of any catalyst, with the bare silica support, and with Ba/SiO_2 in the loading range 10–20 wt%, where the conversions achieved were very low, the selectivities to CH_3Cl approached 5–10%. In what follows all the oxide catalysts supported on silica are denoted, for convenience, as M/SiO_2 where M refers to the metal in the oxide.

The effects of the addition of TCM to the feed stream on conversion and selectivity over alkaline earth oxides supported on silica are shown in Fig. 1. Evidently, the effects were most pronounced on Sr/SiO_2 and

Ba/SiO_2 . A substantial increase in the conversion of methane was observed with both these catalysts. More importantly, a remarkable increase in selectivity to C_2 hydrocarbons and, consequently, a dramatic increase in their yield was observed with these catalysts. On Ca/SiO_2 , on the other hand, the increase in the C_2 selectivity and in the corresponding yield was much less pronounced. On Mg/SiO_2 , the presence of TCM had little effect on either the conversion of CH_4 or on the C_2 selectivity.

The remainder of the report focuses specifically on the results obtained with Ba/SiO_2 .

It is evident from Fig. 2, which illustrates the effect of time on stream on Ba/SiO_2 , for 1.1 Torr of TCM, that in the early periods of time on stream, the conversion drops somewhat while C_2 selectivity increases substantially (both ethylene and ethane selectivity increases). However, after about 3 h of process time, further drops in the conversion were less significant and the C_2 selectivity remains virtually constant.

Table 1 shows the effect of concentration of TCM in the feed on conversion and selectivity. Evidently, at the two lower concentrations of TCM, C_2 selectivity and the corresponding yield obtained at about $3\frac{1}{2}$ h of time on stream are substantially higher than those obtained at approximately $\frac{1}{2}$ h of time on stream, while, at the highest concentration of TCM used, the C_2 selectivity was similar at these two times on stream but the C_2 yield was somewhat lower at $3\frac{1}{2}$ h of time on stream compared to that at $\frac{1}{2}$ h. These trends indicate that relatively longer periods of exposure of the catalyst to CCl_4 are required at lower concentrations of TCM before optimum conditions in terms of C_2 production are obtained. It is also evident from the table that with increasing concentrations of TCM in the feed, the ratio $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ in the C_2 products increases. This suggests that TCM, in addition to enhancing the formation of C_2 hydrocarbons, is catalyzing the dehydrogenation of C_2H_6 to C_2H_4 . It should be emphasized that, un-

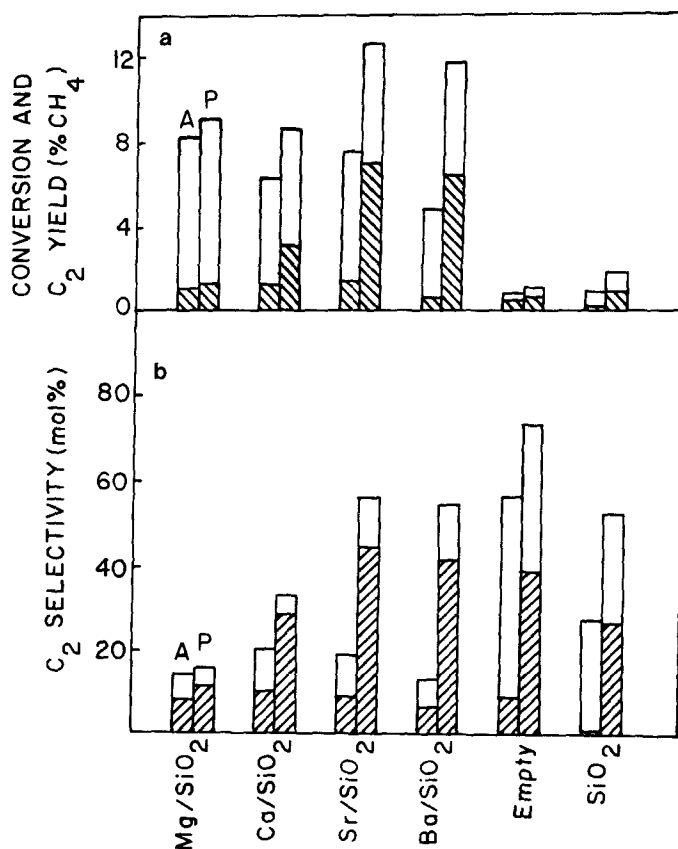


Fig. 1. Conversion, C₂ selectivity, and yield on silica-supported alkaline earth metal oxides (loading = 5.0 wt% metal, data collected $\sim 3\frac{1}{2}$ h time on stream. A and P refer to TCM absent and present, respectively. $W = 1.5$ g, $F = 30$ ml min⁻¹, $T = 775^\circ\text{C}$, $\text{CH}_4 \cong 220$ Torr, $\text{O}_2 = 33$ Torr, $\text{CCl}_4 \cong 1.1 \pm 0.1$ Torr (when present). (a) (▨) CH₄ conversion, (▤) C₂ yield; (b) (▨) C₂H₄, (□) C₂H₆.

TABLE 1

Effect of Concentration of TCM in the Feed on Conversion and Selectivity on Ba/SiO₂^a

TCM conc. (Torr)	Time on stream $\sim \frac{1}{2}$ h				Time on stream $\sim 3\frac{1}{2}$ h			
	CH ₄ conv. (%)	C ₂ selectivity (mol%)	C ₂ yield (%)	$\frac{\text{C}_2\text{H}_4}{\text{C}_2\text{H}_6}$	CH ₄ conv. (%)	C ₂ selectivity (mol%)	C ₂ yield (%)	$\frac{\text{C}_2\text{H}_4}{\text{C}_2\text{H}_6}$
0 ^b	4.8	13	0.60	0.9				
0.60	9.1	33	3.0	1.7	10.4	68	7.1	2.0
1.1	11.1	43	4.8	3.4	11.9	55	6.6	3.1
2.2	11.0	41	4.5	6.6	8.8	39	3.4	4.7

^a CH₄ ~ 225 Torr, O₂ ~ 30 Torr, $W = 1.5$ g, $F = 30$ ml/min., $T = 775^\circ\text{C}$.

^b In the absence of TCM, conversion and selectivities change relatively little with time on stream.

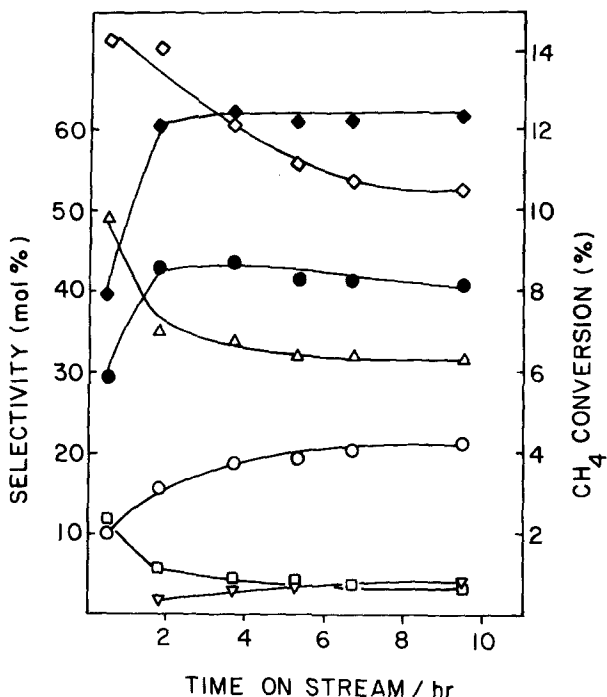


FIG. 2. The effect of time on stream on conversion and selectivity on Ba/SiO₂ in the presence of TCM in the feed. $W = 1.5$ g, $F = 30$ ml min⁻¹, $T = 775^\circ\text{C}$, $\text{CH}_4 \cong 350$ Torr, $\text{O}_2 \cong 65$ Torr, $\text{CCl}_4 = 1.1 \pm 0.1$ Torr. (◇) CH₄ conversion, (◆) C₂ total, (●) C₂H₄, (○) C₂H₆, (△) CO, (□) CO₂, (▽) CH₃Cl.

der all conditions of this study, the actual amounts of C₂ products obtained were more than an order of magnitude higher than the quantity of CCl₄ introduced to the feed. For example, with 0.60 Torr TCM in the feed (Table 1), the ratio of C₂ products obtained to CCl₄ introduced to the reactant stream at 3½ h of time on stream was greater than 25. In what follows the results collected at approximately 3½–4 h of time on stream are reported.

Figures 3–7 illustrate the remarkable enhancement effects of TCM in producing C₂ hydrocarbons from methane over Ba/SiO₂ at several loadings of the catalysts, feed compositions, contact times, and temperatures. In all cases both C₂ selectivity and yield increase dramatically in the presence of TCM in the feed. Furthermore, the proportion of ethylene in the C₂ products was much higher than that of ethane in all cases.

The effect of loading of the catalyst on conversion and selectivity shown in Fig. 3

indicates that, both in the presence and in the absence of TCM in the feed, large conversions of methane, compared to that obtained with the bare support, are observed at a loading of the catalyst as low as 0.6 wt%. In both cases, with increasing loading, the conversion passed through a maximum and then dropped precipitously when the loading exceeded 15 wt%. However, at all loadings in the range 0.6–10 wt%, significant increases in C₂ selectivity as well as C₂ yield are observed on introduction of a small quantity of TCM to the feed stream.

Figure 4 shows that while the conversion increased significantly with increasing residence time both in the presence and in the absence of TCM in the feed, the selectivities to CO_x ($x = 1$ and 2) and to C₂ hydrocarbons remained virtually unaffected. This suggests that CO_x and C₂ hydrocarbons are produced by distinct mechanisms both in the presence and in the absence of TCM in the feed. It may further be noted that the

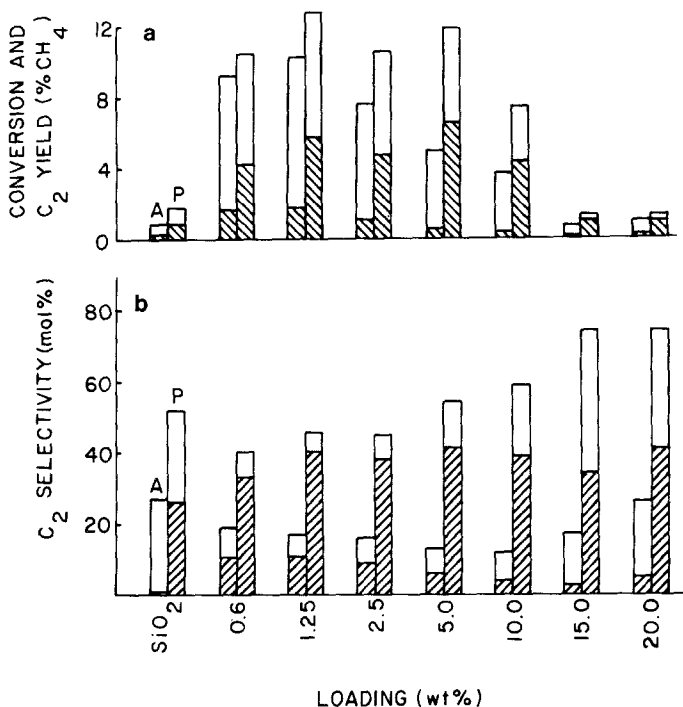


FIG. 3. The effect of loading of the Ba/SiO₂ catalyst on conversion, C₂ selectivity, and yield. A and P represent TCM absent and present, respectively. $W = 1.5$ g, $F = 30$ ml min⁻¹, $T = 775^\circ\text{C}$, $\text{CH}_4 \approx 215$ Torr, $\text{O}_2 \approx 32$ Torr, $\text{CCl}_4 = 1.1 \pm 0.1$ Torr (when present). (a) (▨) CH₄ conversion, (▩) C₂-yield; (b) (▨) C₂H₄, (□) C₂H₆.

specific selectivities to CO and CO₂ in the CO_x fraction and to C₂H₄ and C₂H₆ in the C₂ fraction remained virtually the same, both in the presence and in the absence of TCM, despite a fourfold change in contact time.

The effect of increasing O₂ partial pressure at a constant CH₄ pressure on conversion and selectivity is shown in Fig. 5. Evidently, large increases in conversion as well as in C₂ selectivity are observed at all concentrations of oxygen from the introduction of TCM to the feed and in fact with 13 and 30 Torr of O₂ in the feed the CH₄ conversion, in the presence of TCM, was limited by the availability of O₂. It should be pointed out that in the presence of TCM, while the conversion of CH₄ changed only to a small extent with time on stream at three lower pressures of O₂ used, at the highest pressure of O₂ employed, the conversion decreased substantially (from 35%

after the first ½ h on stream to 20% after 3½ h on stream) (not shown in the figure). The C₂ selectivity, on the other hand, increased by a substantial amount in the first 1–3 h of reaction at all pressures of oxygen examined, as was noted earlier (Fig. 2). It is evident from Fig. 5b that, in the absence of TCM in the feed, the C₂ selectivity progressively drops with increasing concentration of oxygen in the feed, while in its (TCM) presence, a broad maximum is displayed as the concentration of O₂ is increased. The C₂ yield, in the latter case, also appears to show a maximum or to level off with increasing O₂ concentration in the feed. The ratio of C₂H₄/C₂H₆ in the C₂ fraction, in the presence of TCM, changed from 2.3 to 4.9 as the O₂ pressure was increased from 13 to 200 Torr.

With increasing CH₄ pressure, at a constant oxygen pressure, the conversion of

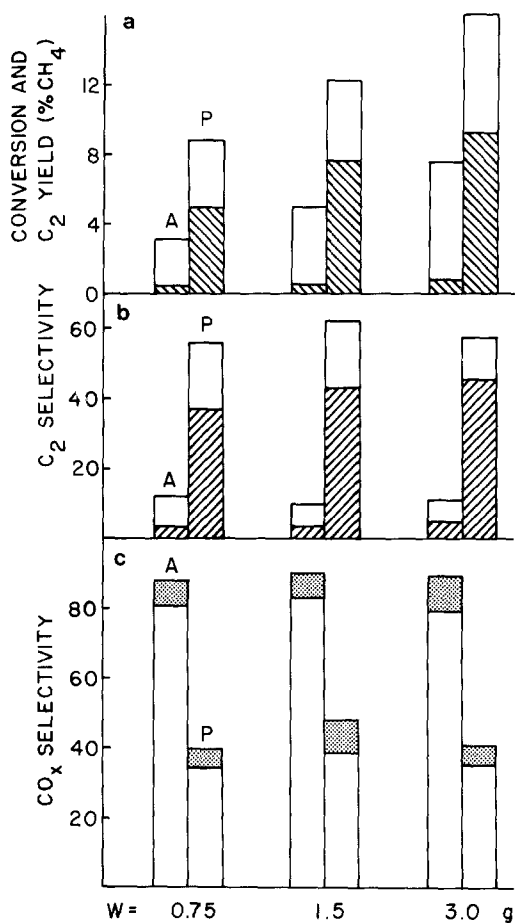


FIG. 4. The effect of time of contact on conversion, selectivity, and yield on 5% Ba/SiO₂. $W = 0.75\text{--}3.0$ g, $F = 30$ ml min⁻¹, $T = 775^\circ\text{C}$, $\text{CH}_4 \cong 350$ Torr, $\text{O}_2 \cong 62$ Torr, $\text{CCl}_4 = 1.1 \pm 0.1$ Torr (when present). (a) (▨) CH₄ conversion, (▩) C₂ yield; (b) (▨) C₂H₄, (□) C₂H₆; (c) (□) CO, (▩) CO₂.

CH₄ dropped both in the presence and absence of TCM, but in the former case, the conversion was substantially higher at any particular pressure of CH₄ in the feed (Fig. 6). With increasing CH₄ pressure in the feed, the C₂ selectivity initially increased substantially and then leveled off to a constant value in the presence of TCM, while in its absence the C₂ selectivity continued to increase gradually. However, at all pressures of CH₄, the C₂ selectivity increased strikingly when TCM was introduced to the

feed. The ratio C₂H₄/C₂H₆ in the products, in the presence of TCM, dropped from 7 to 2 as CH₄ pressure increased from 85 to 475 Torr.

Figure 7a shows that at all temperatures in the range 650–825°C, the conversion of methane was markedly enhanced in the presence of TCM, the relative increase being higher at lower temperatures. Figure 7b illustrates that, while C₂ selectivity increased with temperature both in the presence and in the absence of TCM, it was remarkably higher in the presence of TCM over the entire temperature range studied. It may be noted that although the relative increase in the conversion of methane in the presence of TCM was higher at lower temperatures, the enhanced conversion was rather unproductive as this mainly resulted in the formation of deep oxidation products. On the other hand, at higher temperatures the increased conversion led mainly to the formation of coupled products.

Experiments in which the Ba/SiO₂ catalyst was pretreated with a flow of He + O₂ + TCM mixture and subsequently exposed to a flow of CH₄ + O₂ + He but with TCM absent (after thoroughly purging the system to eliminate TCM from the gas phase) produced CH₄ conversion, C₂ selectivity, and C₂ yield, in the first few minutes of time on stream, comparable to those obtained when TCM was continuously introduced to the reactant stream. However, the effect was temporary and conversion, C₂ selectivity, and yield rapidly dropped to the extent that, within 1–2 h of time on stream, the conversion of CH₄ fell substantially below that which was obtained when the catalyst had not been exposed to TCM. Furthermore, during the periods in which high yields and selectivities to C₂ products were observed, appreciable quantities of Cl₂ were also detected in the effluent. The loss in efficiency of the catalyst for the production of C₂ products in the absence of TCM from the feed stream was coincident with the disappearance of Cl₂ from the effluent.

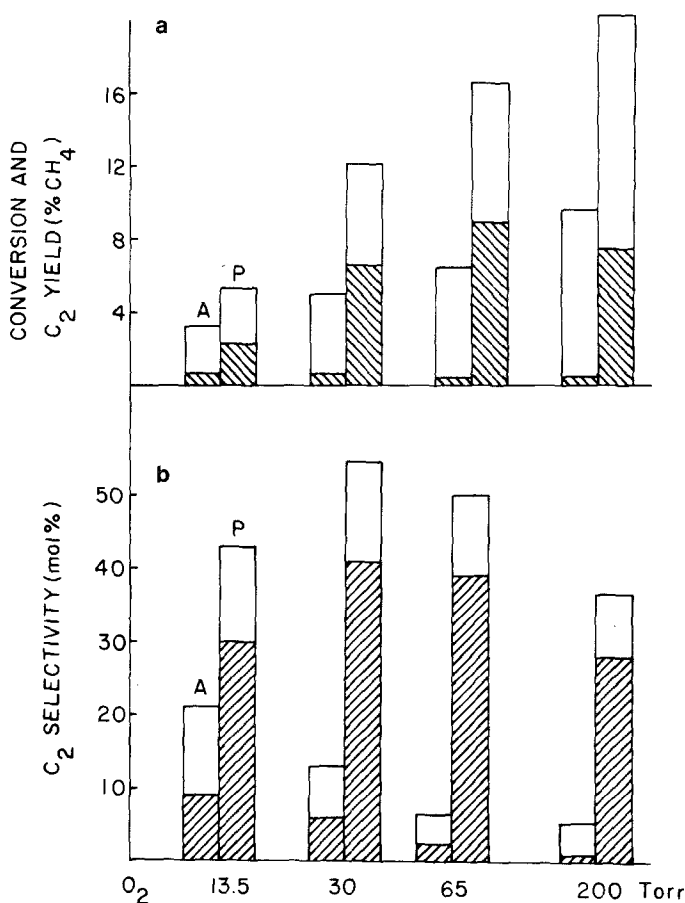


FIG. 5. The effect of increasing pressure of O₂ at a constant pressure of CH₄ on conversion, C₂ selectivity, and yield on 5% Ba/SiO₂. A and P represent TCM absent and present, respectively. $W = 1.5$ g, $F = 30$ ml min⁻¹, $T = 775^\circ\text{C}$, CH₄ = 215 Torr, O₂ = 13–200 Torr, CCl₄ = 1.1 ± 0.1 Torr. (a) (▨) CH₄ conversion, (□) C₂ yield; (b) (▨) C₂H₄, (□) C₂H₆.

These results clearly demonstrate that chlorine in some form is incorporated in the catalyst during the pretreatment stage and is subsequently released as Cl₂ into the gas phase.

DISCUSSION

The present study convincingly demonstrates the advantageous effects of introducing a small quantity of a chlorine-containing compound such as TCM to the feed in the catalytic synthesis of ethane and ethylene, particularly the latter, on alkaline earth oxides supported on silica. Not only was there a remarkable increase in the se-

lectivity to C₂ hydrocarbons but a striking increase in their yield occurred as well. All of the four supported oxides of the alkaline earth series which were examined showed substantial activities both in the presence and absence of TCM. However, the advantageous effects of the addition of TCM were more pronounced with Sr/SiO₂ and Ba/SiO₂ while effects were marginal with Ca/SiO₂ and were almost absent with Mg/SiO₂. Thus, a gradation in the effect of TCM in promoting the coupling of methane was observed in the case of the alkaline earth oxides series. Such a gradation may be related, among other factors, to the basicity

of the oxides which increases in the order $Ba > Sr > Ca > Mg$ and to the strength of interaction of TCM with the oxide surface. The enthalpy of formation of $MgCl_2$ ($\Delta H_f^\circ = -153$ kcal/mole) is substantially lower than that of the remaining three chlorides of this group (-190.0 , -198.0 , and -205.6 kcal/mole (31) for $CaCl_2$, $SrCl_2$, and $BaCl_2$, respectively). If the interaction of the TCM with the catalyst results in the formation of a metal chloride phase, then chlorides of Ba, Sr, and Ca will presumably be more readily formed on the surface than those of Mg. This may account for the relative insensitivity of Mg/SiO_2 to TCM compared

with the remaining catalysts of this series. However, the nature of the active phase is not yet known.

The effect of residence times on conversion and selectivity (Fig. 4) showed that, both in the presence and in the absence of TCM in the feed, the selectivities to CO_x ($x = 1$ and 2) and C_2 hydrocarbons were virtually unaffected by changes in the contact time by a factor of 4, despite substantial changes in the conversion. This suggests that CO_x and C_2 hydrocarbons are produced by independent and distinct mechanisms and there is little subsequent oxidation of C_2H_4 and C_2H_6 into nonselective oxygen-

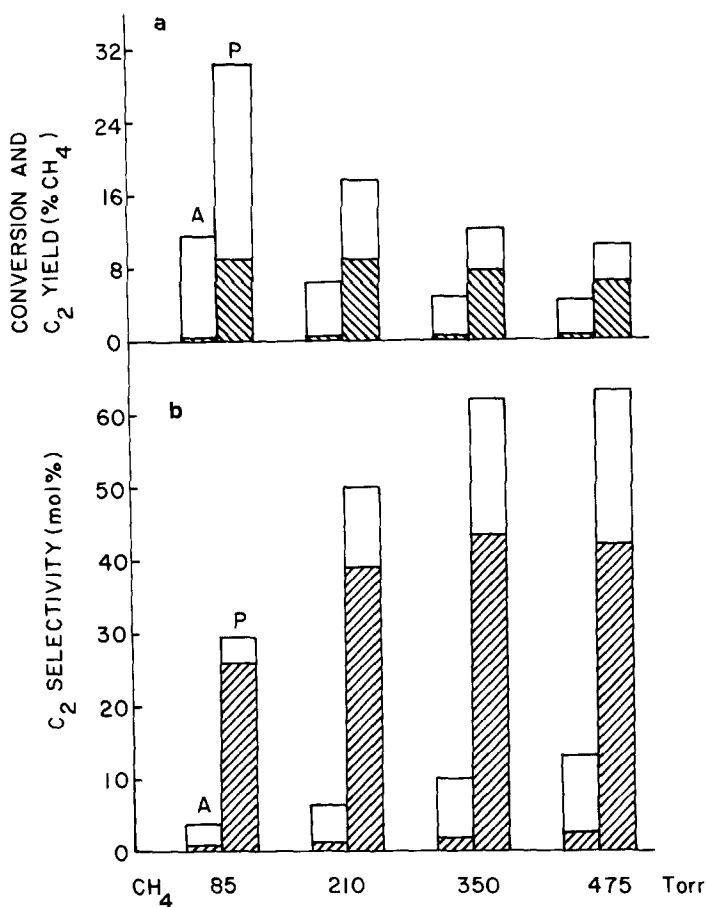


FIG. 6. The effect of increasing pressure of CH_4 at a constant pressure of O_2 on conversion, C_2 selectivity, and yield on 5% Ba/SiO_2 . A and P represent TCM absent and present, respectively. $W = 1.5$ g, $F = 30$ ml min^{-1} , $T = 775^\circ C$, $CH_4 \cong 85-475$ Torr, $O_2 \cong 62$ Torr, $CCL_4 = 1.1 \pm 0.1$ Torr. (a) (▨) CH_4 conversion, (▩) C_2 yield; (b) (▨) C_2H_4 , (□) C_2H_6 .

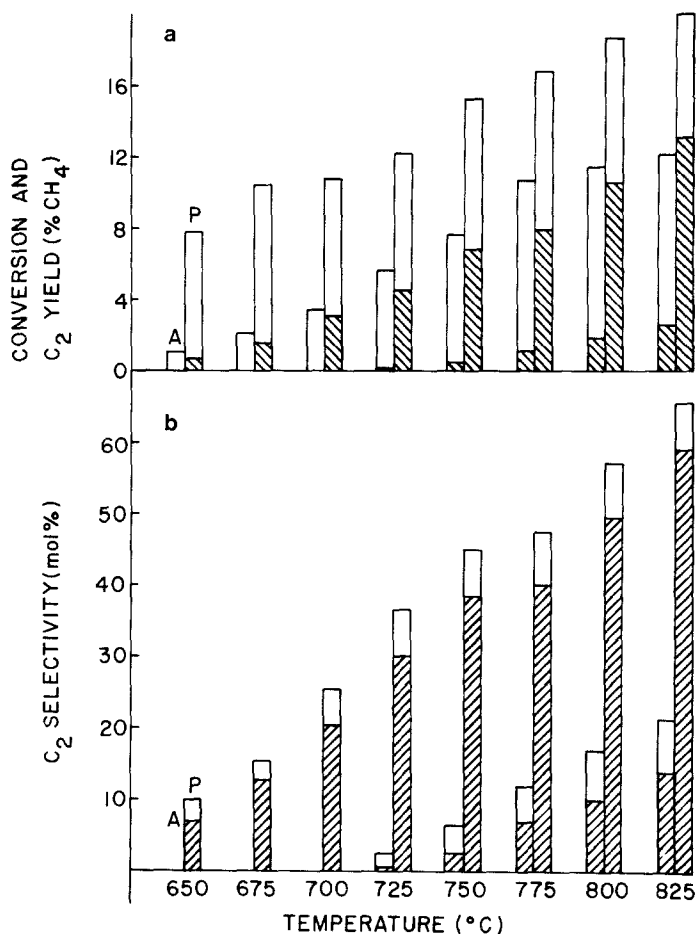
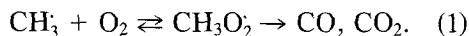


FIG. 7. The effect of temperature on conversion, C₂ selectivity, and yield on 4% Ba/SiO₂. A and P indicate TCM absent and present, respectively. $W = 1.8$ g, $F = 30$ ml min⁻¹, CH₄ = 215 Torr, O₂ = 40 Torr, CCl₄ = 1.1 ± 0.1 Torr. (a) (□) CH₄ conversion, (▨) C₂ yield; (b) (▨) C₂H₄, (□) C₂H₆.

ated products, at least with the low ratio of O₂/CH₄ used in the set of experiments described in Fig. 4.

It has been suggested (4-6, 9, 32-34) that the primary step in the oxidative coupling process is the activation of a methane molecule via abstraction of a hydrogen atom, resulting in the formation of an OH species on the solid surface and in the release of a methyl radical into the gas phase. Ethane is formed by the recombination of methyl radicals in the gas phase, ethylene by the subsequent dehydrogenation of ethane, and CO and CO₂ are produced by the further reactions of methyl radicals with dioxygen,

which may occur both on the surface and in the gas phase:



Many of the features of the reaction reported in this study can be explained within the framework of this model. The unusual decrease in the selectivity to carbon oxides and the increase in the selectivity to C₂ hydrocarbons with increasing reaction temperatures (Fig. 7) can be interpreted as the result of the shift of the equilibrium in process (1) to generate methyl radicals at the expense of methyl peroxy radicals and

hence a decrease in the production of CO_x and an increase in C_2 selectivity.

It should be noted, however, that reaction (1) may not be the only process through which carbon oxides are formed. A variety of surface and gas-phase oxygen species including, but not limited to, mono-oxygen species such as O^- and O^{2-} (lattice oxygen) are available for reaction with the methyl radical to produce unstable intermediates which could subsequently decompose to produce nonselective carbon oxides.

Similarly the decline in C_2 selectivity with increasing partial pressure of oxygen in the reactant stream in the absence of TCM can be related to the increase in the concentration of methyl peroxy radical. In contrast, in the presence of TCM a maximum in C_2 selectivity with partial pressure of oxygen is observed. Although difficult to rationalize, this maximum may be related to the maintenance of the optimum coverage of the surface with oxygen species or to the regeneration of active sites following the oxidation step.

It has frequently been proposed that for a variety of catalysts the activation of a methane molecule via abstraction of a hydrogen is the rate controlling step in the overall reaction. The pretreatment experiments provide firm evidence for the incorporation of chlorine into the catalyst which is subsequently desorbed into the gas phase. It was further shown that the loss of the ability of the catalyst to produce a high yield of C_2 hydrocarbons was coincident with the disappearance of Cl_2 from the product stream. It is therefore tempting to suggest that the chlorine species generated from CCl_4 introduced into the feed is facilitating the methane activation step, thereby producing the remarkable enhancement in the conversion. Indeed, Weilssman and Benson (35) have shown that the abstraction of hydrogen by chlorine atoms from methane and the production of methyl radicals is a rapid process. However, in the present system whether the promotion of this hydrogen ab-

straction step by chlorine species is occurring while it is still present on the catalyst surface or after it is released into the gas phase is difficult to distinguish. Nevertheless, the fact that in the absence of any catalyst, increases in the conversion of methane and C_2 yield by the presence of TCM were very small (Fig. 1) suggests that the catalyst participates directly in this enhancement of the activation process. The observation that the conversion and selectivity to C_2 products are considerably different from catalyst to catalyst (Fig. 1) provides further evidence for the involvement of the solid phase in the conversion process. Perhaps the most conclusive evidence in support of the direct participation of the catalyst is provided from the results of the experiments in which the catalyst is pretreated with TCM. These experiments clearly reveal that the high activity and selectivity of the catalyst for the coupling reaction are maintained only under conditions which ensure the presence of chlorine (in some form) on the catalyst surface. It follows that the incorporation of chlorine in the catalyst alters its characteristics presumably by creating new (or modified) sites for the preferential production of coupling products.

It may be noted that, in addition to the total selectivities to CO_x and C_2 products, the specific selectivities to CO and CO_2 in the CO_x fraction both in the presence and in the absence of TCM, and to C_2H_4 and C_2H_6 in the C_2 fraction in the presence of TCM, were more or less insensitive to residence times. Furthermore, in the present study very high ratios of CO/CO_2 are obtained, in particular under the conditions of limited O_2 availability, in contrast to the relatively low CO/CO_2 ratios reported with other catalysts (5, 6, 9). It should be noted that the CO/CO_2 ratio in the products may be controlled, along with other factors, by the relative concentrations of O_2 and CH_4 in the feed and the ability of the catalyst to oxidize CO to CO_2 and to influence the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$).

As noted earlier, high ratios of C_2H_4/C_2H_6 in the product stream were observed under all conditions of the present study in the presence of TCM. Experiments in which ethane was passed through an empty reactor packed with quartz wool showed that ethane undergoes substantial dehydrogenation producing ethylene at 775°C. The addition of oxygen to the feed stream further enhances this dehydrogenation process. At 700°C in the presence of oxygen in the feed substantial dehydrogenation occurs as well while in its absence conversion of C_2H_6 is quite small. Evidently, at 700°C the dehydrogenation process becomes even more pronounced when TCM is introduced into the reactant stream, both when O_2 is absent from and is present in the feed, while the effect is of lesser significance at 775°C. These results are summarized in Table 2. The table also illustrates that the introduction of the Ba/SiO₂ catalyst has very little influence on this dehydrogenation process regardless of the presence of TCM in

the gas phase. These results suggest that under the conditions used in this report to investigate CH_4 conversion process, 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.* (36) 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 Cl atoms or radicals 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 takes place in the presence of TCM (Fig. 1). Weissman and Benson (35) have shown that at high temperatures

TABLE 2
Homogeneous Conversion of Ethane

Feed	Catalyst ^a	Temp. (°C)	Conversion (%)		Selectivity (mol%)		C_2H_4 yield (%)
			CH_4	O_2	C_1^b	C_2H_4	
$C_2H_6 + He$	None	700	4.1	—	0.8	99.2	4.1
$C_2H_6 + He + O_2$	None	700	44	65	19.5	78.2	34.4
$C_2H_6 + He + TCM$	None	700	10.7	—	3.2	96.8	10.4
$C_2H_6 + He + O_2 + TCM$	None	700	61	85	26.5	72.8	44.4
$C_2H_6 + He$	None	775	36	—	2.0	97.5	35.1
$C_2H_6 + He + O_2$	None	775	75	90	27.2	70.8	53.1
$C_2H_6 + He + TCM$	None	775	38.5	—	2.5	97.5	37.5
$C_2H_6 + He + O_2 + TCM$	None	775	87.5	100	29.3	69.2	60.6
$C_2H_6 + He + O_2$	Ba/SiO ₂ (0.20 g)	700	41.5	55	22.7	75.5	31.3
$C_2H_6 + He + O_2 + TCM$	Ba/SiO ₂ (0.20 g)	700	61.5	90	26.5	71.5	44.0
$C_2H_6 + He + O_2$	Ba/SiO ₂ (0.05 g)	775	74	95	27.4	70.6	52.3
$C_2H_6 + He + O_2 + TCM$	Ba/SiO ₂ (0.05 g)	775	86	100	29	69.5	59.8
$C_2H_6 + He + O_2$	Ba/SiO ₂ (0.20 g)	775	74	95	27	70	51.8
$C_2H_6 + He + O_2 + TCM$	Ba/SiO ₂ (0.20 g)	775	85	100	29.9	68.3	58.1

Note. $F = 30$ ml/min., $C_2H_6 = 57$ Torr, $O_2 \cong 27$ Torr (when present), TCM $\cong 1.2$ Torr (when present).

^a None represents empty reactor packed with quartz wool. The loading of Ba/SiO₂ catalyst was 4-wt% metal.

^b C_1 includes CH_4 , CO , and CO_2 .

chlorine radicals catalyze the formation of C_2H_4 from CH_4 in the gas phase. The participation of chlorine atoms or radicals was also suggested by Otsuka and co-workers (10) and by Anshits et al. (37) to account for the high ratios of C_2H_4/C_2H_6 observed in the oxidative dimerization of methane on NiO and MnO_2 catalysts with added LiCl and on $CaCl_2$ -modified CaO catalysts, respectively. Thus it is possible that, under the conditions of the present study, C_2H_6 is the primary product of the coupling of methyl radicals, as has been concluded from other studies (4, 9, 16, 17), but undergoes rapid thermal and oxidative dehydrogenation to C_2H_4 , a process which is evidently further enhanced by the presence of TCM in the feed.

It was shown that the ratio C_2H_4/C_2H_6 in the products over Ba/SiO₂, in the presence of TCM, increased significantly with increasing O₂ pressure at a constant CH₄ pressure and decreased significantly when the CH₄ pressure was increased at a constant O₂ pressure. This provides some support for the conclusion drawn earlier that ethane is the actual primary C₂ product and ethylene at least partly results from the (oxidative) dehydrogenation of C_2H_6 .

Experiments performed with Ba/SiO₂ catalysts with a range of BaO loading showed that loading as low as 0.6 wt% Ba was sufficient to produce high levels of conversion both in the presence and in the absence of TCM. The conversions remained high up to ~10 wt% Ba and then precipitously dropped when loading exceeded ~15 wt% Ba. The fact that very high levels of conversion are achieved at very low loadings indicates that some oxide-support interactions may exist. The possibility that the active phase is a compound formed from the reaction between BaO and SiO₂ at high temperatures of calcination cannot be ruled out. At high levels of loading this active phase may be partially buried under overlying barium oxide layers causing a precipitous drop in the conversion. How-

ever no direct evidence is presently available to support these interpretations.

In conclusion, this study opens up a viable route for the catalytic oxidative coupling of methane. It is suggested that the chlorine-containing additive promotes the activation of methane on silica-supported SrO and BaO catalysts, although the mechanism of this process is not yet known. Experiments involving pretreatment of the Ba/SiO₂ catalyst provide evidence for the incorporation of chlorine in the catalyst. However, this efficacy disappears unless TCM is continuously fed to the reaction mixture. It is suggested that C_2H_6 is the primary C₂ hydrocarbon product and that ethylene is produced by direct oxidative dehydrogenation of C_2H_6 and that these processes are further enhanced by the presence of TCM. It has been shown that CO_x and C₂ hydrocarbons are predominantly produced by processes independent and distinct from each other. Further studies involving these and other types of catalysts are warranted in order to understand the fundamental aspects of chlorine promotion, to characterize the active phase(s) on the catalyst surface, and to identify catalysts which will produce higher selectivities and yields of C₂ hydrocarbons than those observed in this study. Such studies are currently in progress in this laboratory.

ACKNOWLEDGMENT

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

REFERENCES

1. Lee, J. S., and Oyama, S. T., *Catal. Rev. Sci. Eng.* **30**, 24 (1988).
2. Otsuka, K., Liu, Q., Hatano, M., and Morikawa, A., *Chem. Lett.*, 467 (1988).
3. Gaffney, A. M., Jones, C. A., Leonard, J. J., and Sofranko, J. A., *J. Catal.* **114**, 422 (1988).
4. Ito, T., Wang, J.-X., Liu, C. H., and Lunsford, J. H., *J. Amer. Chem. Soc.* **107**, 5062 (1985).
5. Liu, C. H., Wang, J.-X., and Lunsford, J. H., *J. Catal.* **111**, 302 (1988).

6. Zhang, H. S., Wang, J.-X., Driscoll, D. J., and Lunsford, J. H. **112**, 366 (1988).
7. Burch, R., Squire, G. D., and Tsang, S. C., *Appl. Catal.* **43**, 105 (1988).
8. Carreiro, J. A. S. P., Follmer, G., Lehmann, L., and Baerns, M., in "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 2, p. 891. Chem. Institute of Canada, Ottawa, 1988.
9. Jones, C. A., Leonard, J. J., and Sofranko, J. A., *J. Catal.* **103**, 311 (1987).
10. Otsuka, K., Hatano, M., and Komatsu, T., in "Methane Conversion," Vol. 36 Studies Surf. Sci. Catal." (D. M. Bibby, C. D. Chang, R. F. Howe, and S. Yurchak, Eds.), p. 383. Elsevier, Amsterdam, 1988.
11. Lane, G. S., and Wolf, E. E., in "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips, and M. Ternan, Eds.), Vol. 2, p. 944. Chem. Institute of Canada, Ottawa, 1988.
12. Ahmed, S., and Moffat, J. B., *Appl. Catal.* **54**, 241 (1989).
13. Ungar, R., Zhang, X., and Lambert, R. M., *Appl. Catal.* **42**, L1 (1988).
14. Ueda, W., and Thomas, J. M., in "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 2, p. 960. Chem. Institute of Canada, Ottawa, 1988.
15. Wendt, G., Meinecke, C. D., and Schmitz, W., *Appl. Catal.* **45**, 209 (1988).
16. Asami, K., Hashimoto, S., Shikada, T., Fujimoto, K., and Tominaga, H., *Ind. Eng. Chem. Res.* **26**, 1485 (1987); *Chem Lett.*, 1233 (1986).
17. Hinsien, W., Bytyn, W., in "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 3, p. 581. Dechema, Frankfurt-am-Main, 1984.
18. Tan, S. A., Grant, R. B., and Lambert, R. M., *J. Catal.* **100**, 383 (1986).
19. Grau, J. M., Jablonski, E. L., Dieck, C. L., Verderon, R. J., and Parera, J. M., *Appl. Catal.* **36**, 109 (1985).
20. Cullis, C. F., Keene, D. E., and Trimm, D. L., *J. Catal.* **19**, 378 (1970).
21. Cullis, C. F., and Willatt, B. M., *J. Catal.* **86**, 187 (1984).
22. Eusuf, M., Hasan, A. M., Khan, R., and Choudhury, F. A., *Sci. Res.* **6**, 17 (1969).
23. Eusuf, M., Hasan, A. M., and Khan, R., *Bangladesh J. Sci. Ind. Res.* **10**, 135 (1975).
24. Atlantic Richfield, US Patent **4**, 634, 800 (1987).
25. Schneider, P., and Bergfeld, M., European Workshop on Catalytic Methane Conversion, Bochum, May 1988.
26. Anshits, A. G., Kirik, N. P., Roguleva, V. G., Shigapov, A. N., and Selyutin, G. E., European Workshop on Catalytic Methane Conversion, Bochum, May 1988.
27. Ahmed, S., and Moffat, J. B., *Catal. Lett.* **1**, 141 (1988).
28. Ahmed, S., and Moffat, J. B., *J. Phys. Chem.* **93**, 2542 (1989).
29. Ahmed, S., and Moffat, J. B., *J. Catal.*, in press.
30. Burch, R., Squire, G. D., and Tsang, S. C., *Appl. Catal.* **46**, 69 (1989).
31. Handbook of Chemistry and Physics, 60th ed., 1979-80.
32. Lin, C. H., Campbell, K. D., Wang, J.-X., and Lunsford, J. H., *J. Phys. Chem.* **90**, 534 (1986).
33. Deboy, J. M., and Hicks, R. F., *J. Catal.* **113**, 517 (1988).
34. Lo, M. Y., Agarwal, S. K., and Marcelin, G., *J. Catal.* **112**, 168 (1988).
35. Weissman, M., and Benson, S. W., *Int. J. Chem. Kinet.* **16**, 307 (1984).
36. Burch, R., Crabb, E. M., Squire, G. D., and Tsang, S. C., *Catal. Lett.* **2**, 249 (1989).
37. Anshits, A. G., Kirik, N. P., Roguleva, V. G., Shigapov, A. N., and Selyutin, G. E., *Catal. Today* **4**, 399 (1989).