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Cation Effects in the Oxidative Coupling of Methane on Silica-Supported Binary Alkali and Alkaline Earths

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The oxidative coupling of methane has been investigated with a series of silica-supported binary oxide catalysts containing alkali or alkaline earths or combinations of the former and latter. The conversion of methane and the stability of the silica-supported binary alkali metal oxides were found to increase with decreasing cation mobility, while the selectivities and conversions observed with the binary alkaline earths increase with cation size. The selectivities and conversions of binary alkali/alkaline earths appear to depend upon the size of the alkali and alkaline earth cations, respectively. With small quantities of TCM (CCl_4) added continuously to the feedstream, catalysts containing small alkali and large alkaline earth cations produced the largest selectivities and conversions. © 1993 Academic Press, Inc.

INTRODUCTION

Since the pioneering work of Keller and Bhasin (*1*), the oxidative coupling of methane to more useful chemical feedstock and fuels has been a challenging problem that many industrialized nations have faced (*2*). The ensuing interest in methane conversion to higher hydrocarbons is due to the underutilization of this abundant natural resource and the high costs associated with its transportation, particularly from Alaska and Siberia, where there is a surplus (*3*).

Workers have shown that the conversion of methane and the selectivity to higher hydrocarbons can be enhanced by doping their catalysts with an alkali or alkaline earth metal oxide (*4–6*). As such, a great number of these catalysts have been investigated. Although there have been fewer studies of the oxidative coupling of methane on supported catalysts, of those examined manganese oxide supported on SiO_2 (*4*) and some of the silica-supported alkali/alkaline earth catalysts produced in this laboratory produce acceptable conversion and C_2-selectivity (*7, 8*). In this laboratory a variety of active metal species has been deposited on silica gel. These include alkali (*7*), alkaline earth metal oxides (*8*), and heteropoly oxometalates (*9*), the most active and selective of which have also produced respectable C_{2+} yields.

From a practical point of view the support offers several advantages over that of the pure metal oxide. The thermal stability of the dispersed metal complex may be increased (*10*), and the deposition of the active metal species onto the support generally provides a higher active metal surface area relative to the amount of metal used. Silica gel has many features that make it the support of choice, and it can be purchased almost free of impurities and with very high surface area. In this form, the participation of the support as a catalyst is minimal (*7, 8, 11*) and its surface area allows for a high dispersion-to-weight ratio of the active component. Amorphous silica gels (*12*) are known to maintain their amorphous integrity, but lose surface hydroxyls, surface area, and pore volume as the gel shrinks (*13*), forming a siloxane surface up to ca. 1000°C before rearrangement to another form such as cristobalite takes place. This transformation to another phase is aided by

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mineralizers such as alkali or alkaline earths, in which as the devitrification temperature is decreased interstitial sites are formed by collapsing the Si–O–Si bridges and forming two Si–O$^-$ nonbridging sites. These sites can then be neutralized by two alkalis or one divalent alkaline earth. The diffusion coefficients of the alkali cations decrease with increasing size, and with respect to two alkalis on glasses their decreased cationic mobilities is referred to as the mixed alkali effect (*14*, *15*). The properties directly related to the mobility of the cation show the largest mixed alkali effect. Generally, the diffusion coefficient of the original alkali ion is significantly reduced despite the size of the second alkali. This reduction in mobility varies directly with the second alkali. However, similarly sized or combinations involving smaller alkalis result in larger diffusivities. The reduction of the mobility of the cations as a result of the mixed alkali effect results in higher chemical durabilities with respect to resistance to H_2O/HCl attack and alkali cation–proton exchange. This effect is even more pronounced as a result of high-temperature calcination which further reduces the mobility of the cations as the amorphous glass devitrifies.

In our recent studies, the effect of the gas phase additive TCM has also been examined (*6–8*). It was observed that the addition of a small quantity of TCM in the feed stream increases the higher hydrocarbon selectivity and methane conversion. In light of the beneficial effects of alkali/alkaline earth doping and chloro-additives, we have undertaken an extensive study on the effects of these in the oxidative coupling process using a variety of catalysts. The objectives of this research are to investigate the catalytic properties of binary mixtures of alkali, alkaline earth, and alkali/alkaline earth metal oxides supported on silica gel and to determine the interrelationships between the composition of the supported catalysts and the enhancement effects of TCM.

EXPERIMENTAL

The catalysts used were prepared by simultaneously impregnating the silica gel support (Grace-Davison, grade 407, surface area ca. 740 $m^2\ g^{-1}$) with aqueous solutions of the binary metal acetates or nitrates at 80–90°C followed by drying at 120°C under vacuum (ca. 10^{-3} Torr) for 2 h. The catalysts were finally calcined in air at 750°C for 4 h before charging to the reactor. The quantity of active species laid on the support was calculated to be a 1 : 1 mol% mixture of the two metal salts. This mixture totalled 5 wt% based on the support being 100%. Prior to reaction the samples were calcined *in situ* in an oxygen flow (ca. 25 ml/min) at 775°C for 1 h. For convenience, "wt" is omitted from all future references to these silica-supported binary catalysts.

The catalytic experiments were performed in a fixed-bed continuous flow quartz reactor operated at atmospheric pressure. Details of the reactor design and catalyst packing procedures have been described elsewhere (*6*, *7*). The additive, tetrachloromethane (TCM), was admitted to the main flow of reactants (methane, oxygen, and helium) by passing a separate stream of helium through a gas dispersion tube in a glass saturator containing the liquid at ice-water temperature. The reaction conditions were as follows: $W = 1.5$ g, $F \cong 30$ ml/min, $T = 775$°C, $P(CH_4) \cong 215$ Torr, $P(O_2) \cong 30$ Torr, and $P(CCl_4) \cong 1.1$ Torr; balance to the atmosphere was provided by helium. The reactants and products were analyzed with a Hewlett–Packard 5890A Gas Chromatograph (TCD) equipped with a Molecular Sieve 5A and Porapak T columns. The details and the procedures have been described elsewhere (*6*, *7*).

RESULTS

Silica-Supported Binary Alkali Metal Oxides

Figures 1–3 summarize the results of the silica supported binary alkali metal catalysts. Figure 1 shows the results in the ab-

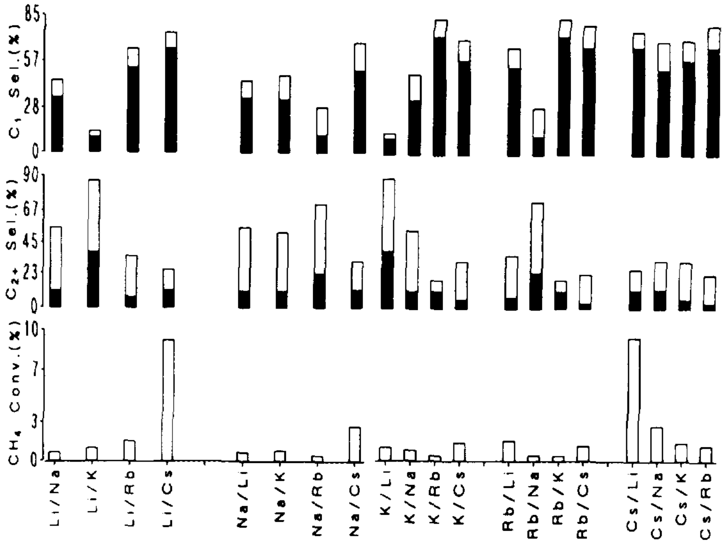

FIG. 1. Oxidative coupling by Group IA/SiO$_2$ catalysts.

sence of TCM for the first 0.5 h on-stream which were studied as the second metal oxide making up a given series was increased to an element of higher atomic weight down the periodic table. The trend in the conversion of methane was most obvious among the Li-containing and Cs-containing catalysts with increases as the differences in the sizes of the alkali metal cations increased. Although the C$_2$ selectivity trends among these two systems were not as salient, they decreased and increased with size differ-

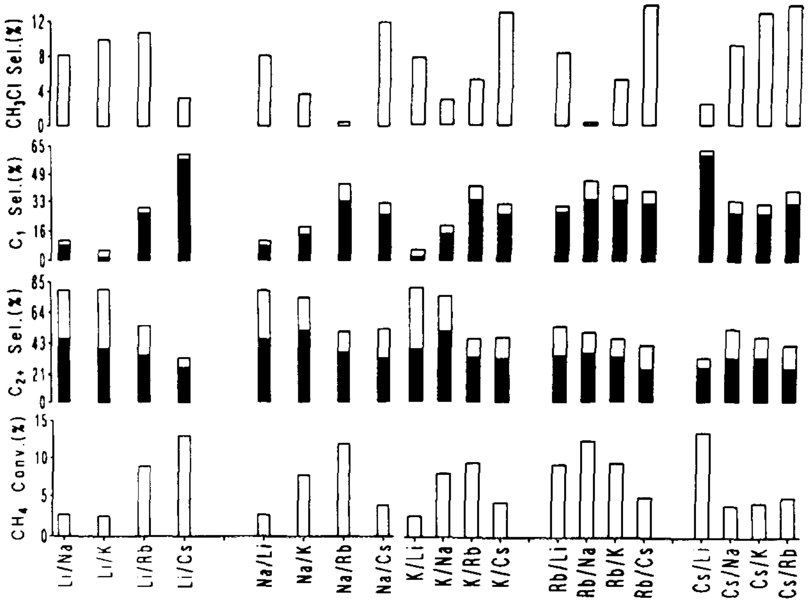

FIG. 2. Oxidative coupling by Group IA/SiO$_2$ catalysts with TCM.

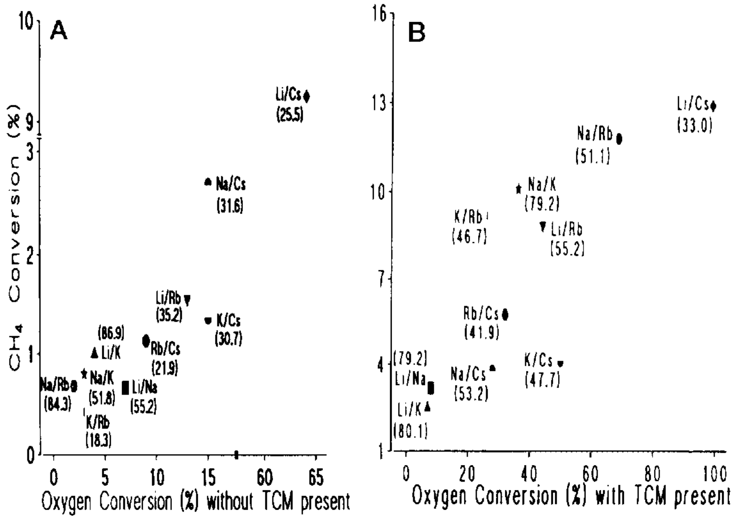

FIG. 3. Methane versus oxygen conversions of Group IA/SiO_2 catalysts. Numbers in brackets refer to C_{2+} selectivity (%).

ence, respectively. The selectivities of some of these catalysts were relatively high. Specifically, the C_2 selectivities of the Li/K, Na/Rb, Li/Na, and Na/K catalysts were 86.9, 84.3, 55.2, and 51.8%, respectively. The results indicated that lower atomic weight alkali metal oxides produced significantly higher selectivities than those with higher atomic weights, particularly those containing Rb and/or Cs.

In the presence of TCM (Fig. 2), after ca. 5 h on-stream (apparent steady state) the above-mentioned trends were again evident. However, the conversion with some of these catalysts showed dramatic improvement as a result of the chloro-additive. The conversions were higher with cations that had a larger size difference, following the order Li/Cs > Na/Rb > K/Rb > Li/Rb > Na/K. The overall order of decreasing C_{2+} selectivity with composition was similar to that found in the absence of TCM with Li/K > Li/Na > Na/K > Li/Rb > Na/Cs > Na/Rb, suggesting that the selectivities were generally greater with lower atomic weight alkali metal oxides. Higher methane and oxygen conversions appeared to result from combinations of low and high atomic weight alkali metal oxides, while generally lower methane and oxygen (Fig. 3A) conversions and higher C_2 selectivities were observed for catalysts containing only low molecular weight alkali metal oxides. This general trend was also observed in the presence of TCM (Fig. 3B).

The activities of the various catalysts were also assessed by following the conversion and selectivity with time-on-stream (Figs. 4A and 4B). The conversions and selectivities of the catalysts generally decreased with time. However, combinations of low and high molecular weight metal oxides were found to be the most stable.

Silica-Supported Binary Alkaline Earth Metal Oxides

Silica-supported binary alkaline earths were compared as the other metal oxide making up that particular series was increased in atomic weight. The catalyst systems were first compared in the absence of TCM (Fig. 5). Interestingly, among these catalysts, great similarity was observed in their selectivities and in their conversions. The highest and lowest selectivities differed by only ca. 8%, while conversions varied

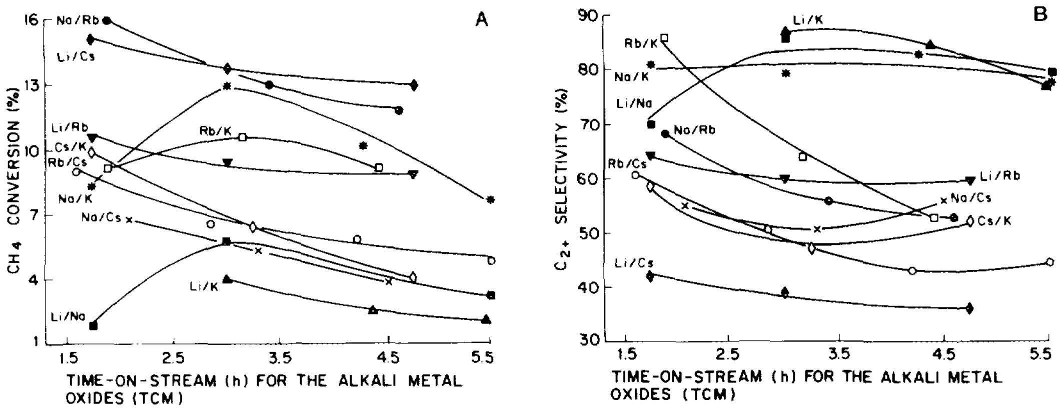

FIG. 4. The effect of time-on-stream on Group IA/SiO_2 catalysts with TCM.

from 6.5 to 10.6%. The selectivities decreased in the order of Ba/Sr > Ba/Ca > Sr/Mg > Sr/Ca > Ca/Mg > Ba/Mg, suggesting, in contrast to the observation with the binary alkali metal oxide systems, that the combination of higher atomic weight metals resulted in higher selectivities.

With TCM present in the feed, (Fig. 6) the selectivities and conversions generally increased by a factor of approximately two. The higher atomic weight Ba- and/or Sr-containing catalysts appeared to be more selective and active compared to the remaining alkaline earth metal oxides examined. The time-on-stream results (ca. 5 h) of the Group IIA metal oxides (Figs. 7A and 7B) showed that these catalysts were more stable than the Group IA metal oxide catalysts. The highest methane conversions were found with those catalysts containing

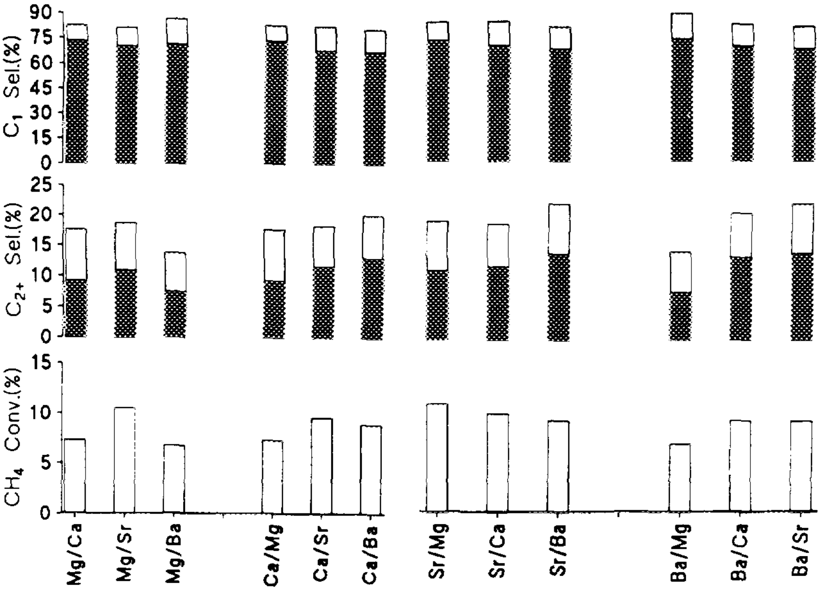

FIG. 5. Oxidative coupling by Group IIA/SiO_2 catalysts.

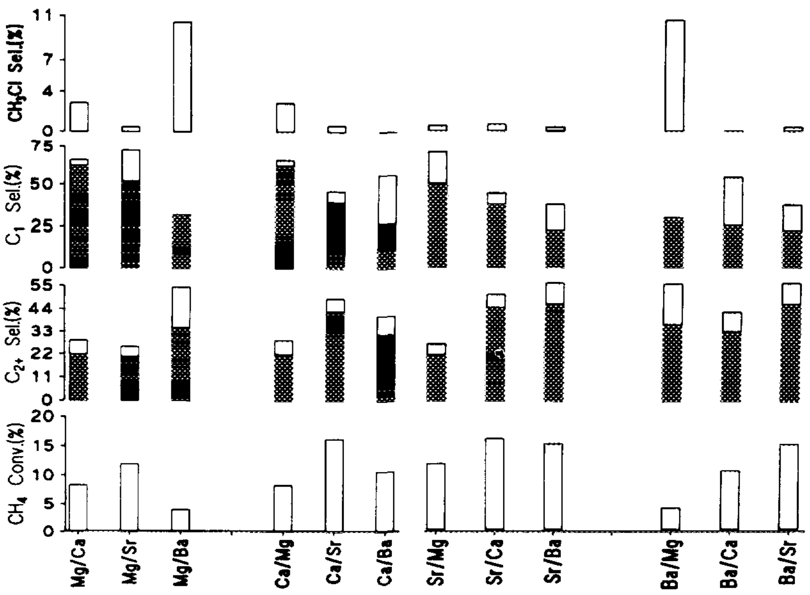

FIG. 6. Oxidative coupling by Group IIA/SiO$_2$ catalysts with TCM.

Sr, whereas higher selectivities were found where Ba was present.

The oxygen conversions (Figs. 8A and 8B) of the Group IIA catalysts whether TCM was present or not were very high and in contrast to the Group IA catalysts, appeared to be independent of the methane conversion. A plot of the selectivity versus methane conversion of the Group IA metal oxide catalysts over time-on-stream (Fig. 9A) indicated that the Li/Cs, Li/Rb, Na/Cs, and Li/K were the most stable catalysts. The Group IIA plot (Fig. 9B) clearly showed the superior stability of these catalysts compared to that of the Group IA catalysts, and the most stable catalysts were found to be silica-supported Ba/Sr and Ca/Mg.

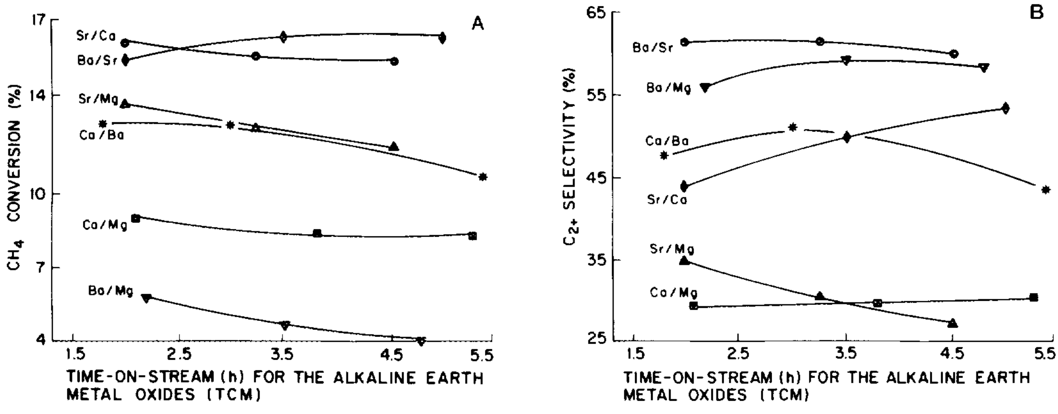

FIG. 7. The effect of time-on-stream on Group IIA/SiO$_2$ catalysts with TCM.

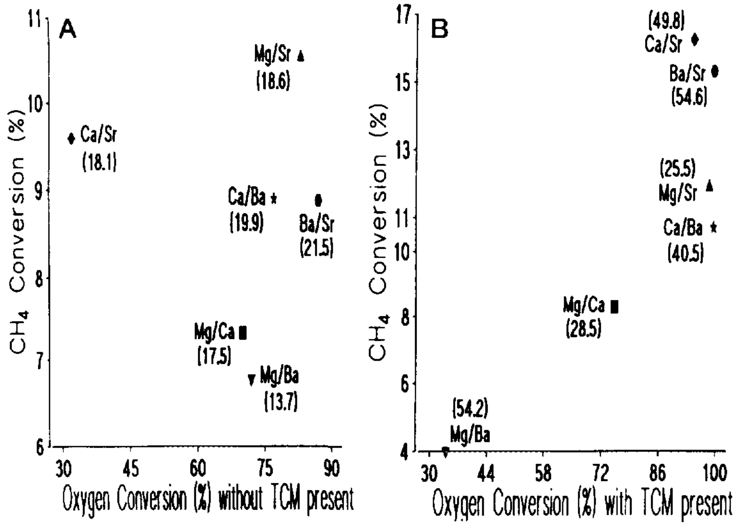

FIG. 8. Methane versus oxygen conversions of Group IIA/SiO_2 catalysts. Numbers in brackets refer to C_{2+} selectivity (%).

Silica-Supported Binary Alkali/Alkaline Earth Metal Oxides

Silica-supported binary oxides containing both an alkali metal and an alkaline earth were also examined. In the absence of TCM (Figs. 10 and 11), the Li-, Cs-, Rb-, and Sr-containing catalysts exhibited the most comparable selectivities. The remaining catalysts (Fig. 10), with the exception of the Li- and Na-containing catalysts, whose selectivities displayed minima, exhibited maxima, sigmoidal, or downward trends with respect to molecular weight of the alkaline earth. The conversions of the catalysts all showed minima, except for the Li-, Na-, Mg-, and Ba-containing catalysts where maxima, upward, sigmoidal, and sigmoidal, respectively, were observed. The Na-containing catalysts' selectivities were highest with Na/Ba > Na/Mg > Na/Ca showing 71.8, 64.6, and 53.9% C_{2+} selectivity, respectively, but lowest among the Cs-

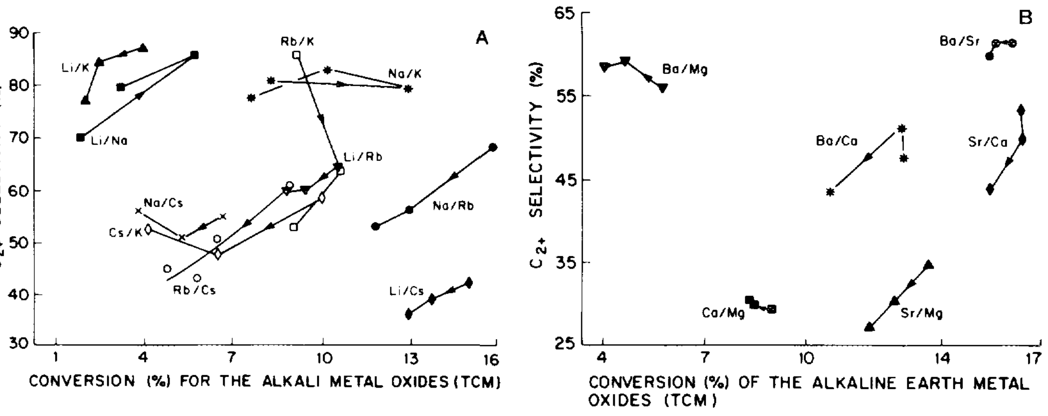

FIG. 9. Selectivity versus conversion of Group IA/SiO_2 and Group IIA/SiO_2 catalysts.

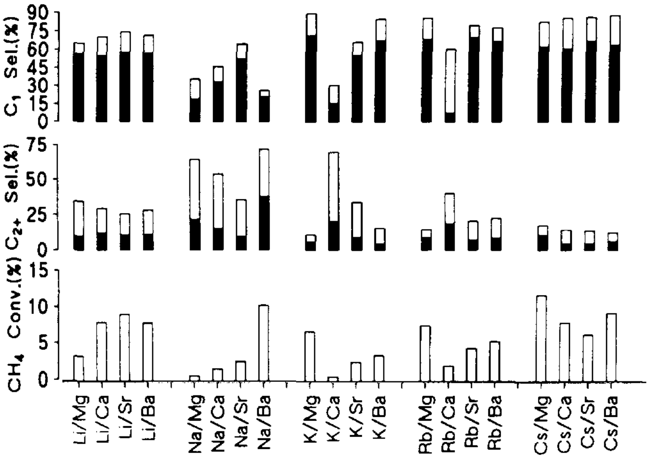

FIG. 10. Oxidative coupling by Group IA/IIA/SiO$_2$ catalysts with respect to Group IA.

containing catalysts, which exhibited less than 20% C_{2+} selectivity. The conversions, although more difficult to categorize, were apparently highest for the Cs-containing catalysts (11.7 to 6.2%) and lowest for a number of Na- and Ca-containing catalysts (as low as 0.5%). The oxygen conversions (Table 1), with the exception of the Li-series which showed a maximum, all exhibited minima.

The addition of TCM to the stream increased both the conversions and C_{2+} selectivities. The results (Figs. 12 and 13) were similar for the Li- and Na-containing catalysts, for which the conversions and selectivities each showed a maximum. The conversions and selectivities of the K-, Mg-, and Ca-containing catalysts showed minima and maxima, respectively. The conversions of the remaining catalysts exhibited minima, and their selectivities were sigmoidally shaped, except for that of the Cs-series which was upward. Comparison of these systems with and without TCM showed that only the trends of the K and Ca systems remained unchanged. Further-

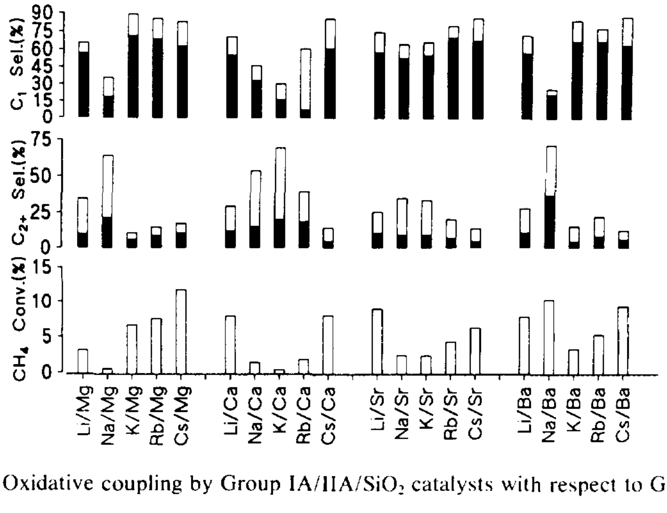

FIG. 11. Oxidative coupling by Group IA/IIA/SiO$_2$ catalysts with respect to Group IIA.

more, the selectivities and conversions were highest with catalysts containing a low-atomic-weight Group IA metal oxide and a high-atomic-weight Group IIA metal oxide. The Li/Sr, Li/Ba, Na/Sr, and Na/Ba catalysts showed conversions of 20.2, 19.2, 20.7, and 16.1%, respectively and their C_{2+} selectivities were found to be 77.1, 76.2, 74.2, and 66.9%, respectively.

The oxygen conversions (Table 1) exhibited minima, except for the Li-containing catalysts (without TCM) and the Na-series that showed a maximum, which was also observed for its selectivities and methane conversions (Fig. 12). The oxygen conversions of the remaining catalysts increased with methane conversion, whether TCM was present or not. Furthermore, some of the K- and Mg-containing catalysts exhibited anomalously higher oxygen conversions in the absence of TCM. The selectivities were found to be lowest for the Mg- and Cs-containing catalysts, which ranged from ca. 25 to 65%. The conversions, excluding the Li-series, were lower among low-atomic-weight Group IA/IIA catalysts. Methyl chloride selectivities (Figs. 12 and 13) were lowest for the Li-, Cs-, and Ba-

TABLE 1

Oxygen Conversions of Binary Alkali/Alkaline Earth Metal/SiO_2 Catalysts

Catalyst	Conversion (%)			
	No TCM[a]		TCM[b]	
	Methane	Oxygen	Methane	Oxygen
Li/Mg	3.1	25	15.9	99
Li/Ca	7.8	52	16.6	99
Li/Sr	8.9	62	20.2	96
Li/Ba	7.8	56	19.2	99
Na/Mg	0.5	7	1.8	9
Na/Ca	1.4	2	14.1	77
Na/Sr	2.4	11	20.7	99
Na/Ba	10.3	42	16.1	95
K/Mg	6.6	54	2.2	22
K/Ca	0.4	2	1.7	2
K/Sr	2.3	7	4.8	6
K/Ba	3.3	20	9.5	40
Rb/Mg	7.7	68	3.9	33
Rb/Ca	1.8	1	3.5	10
Rb/Sr	4.3	28	7.1	43
Rb/Ba	5.3	40	9.1	49
Cs/Mg	11.7	85	10.8	78
Cs/Ca	7.9	65	10.8	69
Cs/Sr	6.2	47	13.9	93
Cs/Ba	9.3	80	13.9	99

[a] Within 30 min time-on-stream.

[b] Apparent steady state between 4 and 5.5 h time-on-stream.

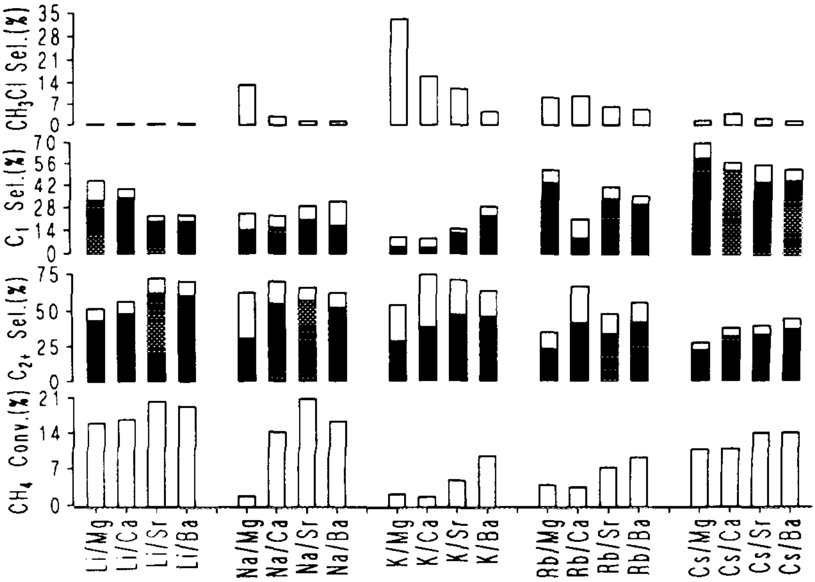

FIG. 12. Oxidative coupling by Group IA/IIA/SiO_2 with respect to Group IA (with TCM).

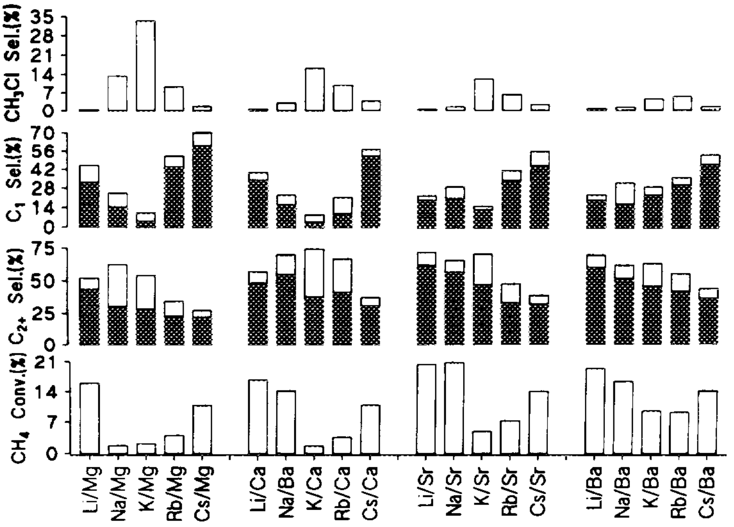

FIG. 13. Oxidative coupling by Group IA/IIA catalysts with respect to Group IIA (with TCM).

containing catalysts and highest for the K-, Mg-, and Rb-containing catalysts.

The selectivity versus conversion plot for various times-on-stream (Fig. 14) with the alkali/alkaline earth series catalysts demonstrated that the deactivations were not as apparent as those with the Group IA catalysts, but were similar to those of the Group IIA catalysts. Interestingly, the most active and selective catalysts (upper right hand corner of the plot) exhibited positive slopes, resulting in an almost proportional deactivation of their selectivities and conversions. Also, these more active catalysts demonstrated very high stabilities compared to the various combinations of Group IA and Group IIA metal oxides. Mixtures of some of the larger alkali and smaller alkaline earth cations, i.e., Cs/Ca, Rb/Mg, and K/Mg, resulted in negative slopes, and mixtures in which both cations were large, i.e., Cs/Ba, Cs/Sr, Rb/Ba, and K/Ba, resulted in relatively stable catalytic behaviour. The results indicated that combinations of a low-atomic-weight alkali metal and a high-atomic-weight alkaline earth oxide supported on silica resulted in the highest conversion (ca. 20%) and selectivities (ca. 77%), and their chlorinated by-products were either undetected or in trace amounts. Furthermore, catalyst deactivation was not as apparent for these catalysts.

DISCUSSION

The present report demonstrates the significance of the silica supported binary cat-

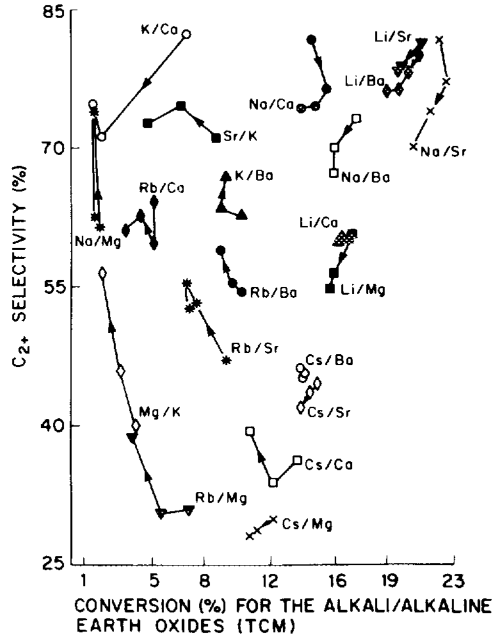

FIG. 14. The effect of time-on-stream on Group IA/IIA catalysts.

alyst compositions with respect to Group IA and/or Group IIA cations. In the presence of TCM, the most active and selective catalysts were those comprised of a small alkali and large alkaline earth.

As noted in the Introduction, the surface area of silica gel is known to decrease when exposed to high temperatures. This has been attributed to its bulk and surface dehydration in which the length of the pores decrease as do the number of pores. Mineralizers such as low-molecular-weight alkali metals promote this transition at much lower temperatures (*13*). Thus it is important to discuss the importance of surface area in the context of the present work. Illustrative values of the surface areas of a silica-supported alkali metal, alkaline earth, and an alkali metal/alkaline earth are shown in Table 2 both for the fresh and used samples. As expected, both heating and impregnation of the silica result in considerable reduction in the surface areas. In almost all cases the surface areas of the silica-supported catalysts are small and there is no evidence of a direct correlation between surface area and catalytic properties.

Although silica gel has been shown to catalyze the oxidation of methane to formaldehyde at reaction temperatures between 500 and 600°C (*7*, *8*, *11*), since the conversions are relatively small it is expected that the direct participation of the support in the oxidative coupling process is insignificant, although the indirect role of silica gel cannot be discounted.

TABLE 2

Surface Areas of Typical Catalysts

Catalyst	Surface area (m^{2}g)	
	Fresh	Used
Silica gel	750.6	286.5[a]
Li/SiO$_2$	22.9	9.5
Ba/SiO$_2$	225.7	3.9
Li/Sr/SiO$_2$	5.0	0.4
Na/Sr/SiO$_2$	9.8	3.4

[a] After typical loading conditions but in the absence of a loaded catalyst.

It should be noted that XRD patterns showed that the amorphous character of the silica was little affected by the loading process. However, as alluded to elsewhere in this report, phases are observed which provide evidence for the formation of species resulting from the interaction of the support and the supported material. The work of Tadros and Lyklema (*18*) as well as that of Abendroth (*19*) has shown the importance of the pH of the silica gel solution with respect to the adsorption of alkali and/or alkaline earth metal salts. Since most of the present catalysts were prepared in mildly acidic solutions ($5 < \mathrm{pH} < 6$) some preferential adsorption of the cation to the silica surface is to be anticipated, but this is not expected to unduly bias the present results.

Researchers have shown that by doping a catalyst with an alkali or alkaline earth the basicity of the surface is increased, which results in higher selectivity and conversion over that of the undoped catalyst (*5*, *6*). However, if the reaction depended solely on the basic strength of the catalyst, then supporting two of the most basic species, i.e., Rb/Cs, should result in high activity, but this was not observed among the catalysts studied. In the absence of TCM (Fig. 1), the results showed that much higher conversions were observed when there was a larger size or mass difference between the two cations. On the basis of the mixed alkali effect (*14*, *15*), there appears to be an inversely proportional relationship between the mobility of the cations and the conversions. Similarly, there is a directly proportional relationship between increased alkali mobility and selectivity. In other words, catalysts in which both cations are large, i.e., the Cs-containing catalysts and the larger combinations involving K- and Rb-containing catalysts, showed high conversions as opposed to combinations involving smaller cations that are known to possess higher mobilities throughout the silica network (*16*, *17*). At apparent steady-state (with TCM in the feed, Fig. 2) only the Li and to a certain extent the Na- and Cs-containing catalysts conformed to the mixed alkali effect. The inability to correlate the intermediate sized mixtures may be related to the dissimilar trends towards deactivation of the catalysts. For example, a comparison of the Rb/K and the Cs/K catalysts shows that the selectivity of the former decreased ca. 30% although its conversion remained essentially constant, while that of the latter decreased by ca. 6% and its selectivity decreased by ca. 4%. These extreme differences in deactivation may be related to the varying affinities of the particular cations of the silica surface (*18*, *19*) and to their crossover point (point at which they have equal mobility) that varies from mixture to mixture. Factors such as coordination of the cations, and the rate of oxygen incorporation into the lattice could also play a role. The Rb/Cs, Cs/K, and Rb/K catalysts exhibited almost complete combustion of methane. This was probably due to a high rate of oxygen activation on the surface and a slow rate of oxygen incorporation into the lattice that would result in a greater concentration of weakly bound surface oxygen (*20*). The Li/Cs, Li/Rb, Na/Cs, and Li/K catalysts showed the highest time-on-steam (5 h) stability of all the catalysts (Fig. 4). This phenomena can also be associated with the mixed alkali effect, in which the chemical durability is higher among cations with lower mobilities, resulting in a higher resistance to H_2O/HCl attack, which are by products of this catalytic process. Similarly, Gokhberg *et al.* (*21*) recently demonstrated that the resistance to HCl attack over silica-supported alkali metals increased with the size of the alkali metal cation, in which cation mobility decreased with increased size of the cation.

The binary alkaline earth catalysts (in the absence of TCM) which were more active and less selective than those formed from alkali metals, exhibited little change in selectivity and conversion from catalyst to catalyst. However, with TCM (Fig. 6), the conversion and selectivity for some catalysts increased by ca. twofold. The enhancements were centred around combinations of larger cations, Ba/Sr, Ba/Ca, and Sr/Ca, making the conversions and selectivities more dependent on the basicity, which was also a factor for a series of silica-supported alkaline earth oxides in which the order of deceasing selectivity and conversion was Ba > Sr > Ca > Mg (*8*). This behaviour could, in part be related to their similar coordination to oxygen as found in oxide glasses (*22*), and their greater bond strengths to oxygen with respect to the Group IA metal oxides, hence making them more equally susceptible to coordination with H_2O or oxygen, less likely to migrate and the process more dependent on their ability to donate electrons, i.e., their basicity.

The activities and selectivities of Mg/Ca and Ba/Sr showed very little change over time compared to the rest of the binary alkaline earth catalysts. This phenomenon could be due to the relative sizes of the two cations making up the catalyst since their divalent character might make them more dependent on the structural orientation of the nonbridging oxygen sites. Consider the surface of a Mg/Ba catalyst consisting of very large and very small sites that accommodate the cations. Upon excitation that could instigate ion migration, the cation either binds onto another site or is lost from the surface. It is much easier for similarly sized cations to occupy each other's sites and for the silica to conform in order to accommodate either cation, thereby resulting in longer time-on-stream stability. This phenomenon was not observed with the alkali metals probably because they are monovalent and two are required to neutralize the two nonbridging oxygen species to maintain electroneutrality, so that even if a metal cation is very large a much smaller proton can neutralize the other negative oxygen species. Comparison of the time-on-stream stabilities between these two groups showed that the least stable Group IIA catalysts were as stable as the most stable Group IA catalysts, suggesting that the stronger metal–oxygen bonding present among the group IIA catalysts provides for the longer on-stream stability of the catalyst. Furthermore, Ahmed and Moffat (*8*) showed that after ca. 6 h on-stream, the conversion of Ba/SiO_2 decreased from ca. 14 to 10%, whereas the most stable mixed alkaline earth catalysts reported here exhibited essentially constant selectivity and conversion over time. These results suggest that mixing alkaline earths could result in increased stability as observed in the mixed alkali effect.

With TCM in the feed (Figs. 12 and 13), the results of supporting a binary alkali/alkaline earth catalyst showed that the individual traits of the binary alkali and binary alkaline earths mentioned in the preceding sections were preserved. The selectivities appear to be influenced by the size of the alkali and the conversions by that of the alkaline earth. Therefore, the highest selectivities (small alkali) and conversions (large alkaline earth) were observed with Li/Ba, Li/Sr, Na/Sr, Na/Ba, and Na/Ca catalysts. There were also similar effects observed with Cs/Ba, Cs/Sr, Cs/Ca and Cs/Mg that were somewhat active and non selective and, Na/Mg and K/Ca that were selective and not very active.

The stability was found to be greater among catalysts containing larger alkali/alkaline earth metal cations (lower cationic mobility because of the larger cations) and among small alkali/large alkaline earth metal cations (probably due to increased crystallization of the support) and lowest among the K/Mg, K/Ca and Na/Mg catalysts (Fig. 14). Some of these catalysts showed negative slopes over time in which the selectivity to C_{2+} hydrocarbons and CH_3Cl increased as the conversion decreased, suggesting that an active chlorine phase was slowly binding to the surface. The addition of TCM appears to convert certain active sites from nonselective (increased C_{2+} selectivity from 10 to 40% for some Cs-containing catalysts) to more selective ones. For some catalysts the oxygen as well as the methane conversions were observed to decrease by the addition of TCM (at apparent steady state). This phenomenon was also observed with silica gel, in which the conversion decreased when TCM was added. These results suggest that the active chlorine species are competing with methane or oxygen for the active site or that the chlorine species is poisoning the active site. Generally, the addition of TCM to the stream had a more pronounced effect on the C_{2+} selectivities than on the conversions. This could be attributed to the chlorine species adsorbing onto the active site, which would reduce the concentration of weakly adsorbed surface oxygen species and increase the selectivity. This view was described earlier for the Cs-containing alkali metals. While at this time the mechanism through which TCM participates in the methane conversion process is not known, recent studies of the oxides of cerium, lanthanum, praseodymium, and samarium as catalysts in this reaction have provided evidence for the formation of and participation by the oxychlorides of these elements (*23*). From a purely practical viewpoint, the presence of any species containing chlorine is obviously undesirable. However, two factors mitigate against these objections, namely, the relatively small quantities of chlorine present and the observation that much, if not all, of the chlorine observed in the product stream exists in the form of hydrogen chloride.

The oxygen and methane conversions (Table 1) showed some very interesting catalytic trends that appear to be dependent on the cationic radii of the atoms. The Li-containing catalysts showed methane and oxygen conversion trends that were at a maximum with Li/Sr. These trends could be attributed to the size of the ionic radii, which occupy Si–O nonbridging oxygen sites (*12*), in which 2 Li^+ and Sr^{2+} can more easily interchange because of their similar radii. The Na/Mg catalyst, in which $r_{Na} >$

r_{Mg}, exhibited little change in oxygen conversion as a result of TCM addition and very low methane conversions even with TCM present. However, with increasing size of the alkaline earth the activity increased. This trend was observed with the remaining alkali/alkaline earths in which combinations involving larger alkalis and smaller alkaline earth metal cations resulted in oxygen conversions that were greater without TCM. These findings emphasize the importance of the size ratio of the cations with respect to the active site and its bearing on the catalysts.

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