

# The Active Phase in Sodium-Doped Calcium Oxide Catalysts for Oxidative Coupling of Methane

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The reactivity of pure and sodium-promoted calcium oxide catalysts toward the oxidative coupling of methane at 640°C has been investigated. While the pure calcium oxide was essentially a combustion catalyst, sodium-promoted calcium oxide exhibited significant C<sub>2</sub> productivity. Study of the deactivation of both pure and promoted catalysts demonstrated that the presence of calcium oxide was necessary for both catalysts to be active. This observation, combined with the effects of sodium doping on C<sub>2</sub> selectivity, suggests that the active phase on Na/CaO catalysts toward C<sub>2</sub> formation consists of sodium species associated with calcium oxide. This active phase was destroyed when calcium oxide was converted into calcium carbonate under reaction conditions. © 1991 Academic Press, Inc.

## 1. INTRODUCTION

The activity of metal oxide catalysts toward methane oxidative coupling can generally be promoted by doping alkaline metal ions. For the catalyst systems of Li/MgO (1, 2), Na/CaO (3), and Li/ZnO (4), Lunsford and co-workers have attributed this promotive effect to the formation of O<sup>-</sup> centers through substitution of alkaline metal ions into the oxide lattice. In a study of Li-, Na-, and K-promoted CaO catalysts by Carreiro and Baerns (5), the incorporation of the alkaline metal ions into CaO surfaces was also believed to be responsible for the improved C<sub>2</sub> selectivity, although the mechanism of promotion was attributed to an increase in the basicity of the oxide. Iwamatsu *et al.* (6) have attributed the promotive effect observed from Na<sup>+</sup>- and Rb<sup>+</sup>-doped MgO catalysts to lattice distortion. Despite the different natures of active centers proposed, the cooperation of alkaline metal ions and oxide substrates appears to be the common element for these catalysts to be active and selective toward oxidative coupling of methane.

The effect of lithium doping on the reactivity of MgO catalysts has been studied recently in this laboratory (7). The catalysts

doped with lithium exhibited a much higher activity toward oxidative coupling of methane than pure MgO samples. These catalysts exhibited a characteristic O(1s) peak at 533.0 eV upon treatment under the reaction conditions that has been assigned to the O<sup>-</sup> center formed by substitution of Li<sup>+</sup> ions into MgO lattices. A good correlation between the concentration of this species and CH<sub>4</sub> conversion has been observed, suggesting that the O<sup>-</sup> center is responsible for methane activation.

The present paper describes the results of X-ray photoelectron spectroscopy (XPS) measurements combined with reaction kinetics measurements in a study of sodium-promoted calcium oxide. The unpromoted CaO was active for methane conversion although the selectivity toward coupling products was very low. The presence of sodium promoter did not appreciably increase the activity of the catalyst, but did substantially enhance the selectivity toward C<sub>2</sub> hydrocarbon formation. The selectivity pattern is strong evidence for the presence of two types of sites on Na/CaO catalysts: nonselective (CO<sub>x</sub>-forming) sites associated with the pure CaO surface and selective (C<sub>2</sub>-forming) sites associated with the sodium-promoted CaO surface. Unlike in the Li/

MgO catalyst system and in the Na/CaO catalyst system in the literature reports, here rapid deactivation of the catalysts was observed. This deactivation was found to be a sensitive function of reaction conditions, both  $\text{CH}_4 : \text{O}_2$  ratio and temperature. Deactivation correlated with the formation of calcium carbonate and the disappearance of free calcium oxide on the surface. The deactivation results demonstrate the necessity of maintaining oxide surface available to the reaction mixture. This requirement provides insight into the nature of sites of methane activation.

## 2. EXPERIMENTAL

Experimental details for this study were similar to those reported previously for Li/MgO catalysts (7). Sodium-promoted calcium oxide catalysts were prepared by dissolving  $\text{Na}_2\text{CO}_3$  (Aldrich, 99+ % purity) in deionized water and mixing with CaO powders (Aldrich, 99.95% purity). The resulting slurry was heated on a heating plate into a paste-like finish, dried at  $130^\circ\text{C}$  in an oven, and then ground into powder. Pure calcium oxide catalysts were prepared in a similar manner. The sodium loading is defined as the ratio of the weight of sodium to that of sodium plus calcium oxide. The reaction was carried out in a fixed-bed reactor consisting of quartz tubing and a gold bucket liner. The gold bucket was used to hold catalysts and prevent alkali metals from migrating onto the walls of the quartz reactor, which were then active for methane conversion. Unless otherwise specified the kinetic results reported here were all obtained with 1 g of catalyst at  $640^\circ\text{C}$  using a continuous reactant feed of 175 Torr  $\text{CH}_4$ , 90 Torr  $\text{O}_2$ , and 495 Torr He at a total flow rate of 50 ml/min, and catalyst samples were pretreated prior to starting reaction in an  $\text{O}_2$  stream (60 ml/min) at  $650^\circ\text{C}$  for 1 hr. In the absence of catalyst, methane conversion was negligibly small, less than 1.5%. Gas chromatography with a thermal conductivity detector was used to analyze reaction products. Catalyst surface area was measured with an Omni-

sorp 360 BET apparatus and a BET apparatus in the Amoco Research Center.

A VG ESCALAB/SIMSLAB was used to analyze the composition of catalyst surfaces. This instrument featured a high pressure cell attached to the vacuum system. Catalyst samples, pressed into thin wafers and mounted on a holder with gold foil, were treated in the cell under various pretreatment and reaction conditions and then transferred into the analytic chamber for XPS measurements without exposure to atmosphere. The catalyst samples in this study were all subject to electrostatic charging, resulting in the shift of XPS peak positions. The  $\text{C}(1s)$  peak of residual carbon, present on all sample surfaces, was assigned a binding energy of 284.9 eV and used as the binding energy reference throughout this work. With this reference, a pure commercial  $\text{Na}_2\text{CO}_3$  sample exhibited a  $\text{C}(1s)$  peak at 289.4 eV, an  $\text{O}(1s)$  peak at 530.9 eV, and an  $\text{Na}(1s)$  peak at 1070.5 eV. The  $\text{C}(1s)$ ,  $\text{O}(1s)$ , and  $\text{Ca}(2s)$  peaks from a pure  $\text{CaCO}_3$  sample, prepared by reacting CaO powders with  $\text{CO}_2$  in the high pressure cell at  $640^\circ\text{C}$ , were at 289.7, 531.1, and 438.8 eV, respectively. The  $\text{C}(1s)$  and  $\text{O}(1s)$  binding energies from these standard carbonate samples, along with those from the literature and those from the other samples under study, are listed in Table 1. While the discrepancy in absolute binding energies between our standard carbonate samples and those in the literature may result from the uncertainty introduced by referencing to the residual carbon peak, the difference between the carbonate  $\text{O}(1s)$  and  $\text{C}(1s)$  peaks from our carbonate samples (ca. 291.4 eV) is consistently smaller than that from the literature (291.8 to 292.1 eV) for unknown reasons. (The energy scale of our XPS instrument has been calibrated frequently with  $\text{Au}(4f)$ ,  $\text{Ag}(3d)$ , and  $\text{Cu}(2p)$  emissions. Note also that a difference of 291.5 eV was observed from lithium carbonates on Li/MgO samples in this laboratory (7)). In order to quantify the surface composition, the sensitivity factors for  $\text{O}(1s)$ ,  $\text{C}(1s)$ ,  $\text{Na}(1s)$ , and  $\text{Ca}(2s)$  emissions were

TABLE 1

Sample	Binding energy	
	C(2s) (eV)	O(1s) (eV)
Standard CaCO <sub>3</sub>	289.7	531.1
Standard Na <sub>2</sub> CO <sub>3</sub>	289.4	530.9
CaCO <sub>3</sub> <sup>a</sup>	289.4	531.2
CaCO <sub>3</sub> <sup>b</sup>	289.6	531.4
CaO <sup>c</sup>	—	529.4
Na <sub>2</sub> CO <sub>3</sub> <sup>d</sup>	289.4	531.5
Na ox <sup>e</sup>	—	529.7
CaO in O <sub>2</sub> -treated CaO catalyst	—	528.5 to 528.7
CaCO <sub>3</sub> in CaO Catalyst upon reaction	289.6 to 290.0	531.0 to 531.5
CaO in O <sub>2</sub> -treated 0.5-wt% Na/CaO	—	528.1 to 528.5
CaCO <sub>3</sub> in 0.5-wt% Na/CaO upon reaction	289.5 to 289.6	531.0 to 531.1

<sup>a</sup> Ref. (8).<sup>b</sup> Ref. (9).<sup>c</sup> Ref. (10).<sup>d</sup> Ref. (11).<sup>e</sup> Ref. (12).

calibrated with the pure CaCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> samples. The measured sensitivity factors are listed in Table 2 along with those from the literature (13).

### 3. RESULTS

The structure of this investigation was shaped by two features of the catalysts under study, which are represented by the kinetic data from a pure and a 0.5-wt%-Na-

TABLE 2

Sensitivity Factors for the O(1s), C(1s), Na(1s), and Ca(2s) Emissions<sup>a</sup>

Emission	Sensitivity factor	
	This work	Ref. (13)
O(1s)	1.00	1.00
C(1s)	0.36	0.38
Na(1s)	2.73	3.48
Ca(2s)	0.70	0.71

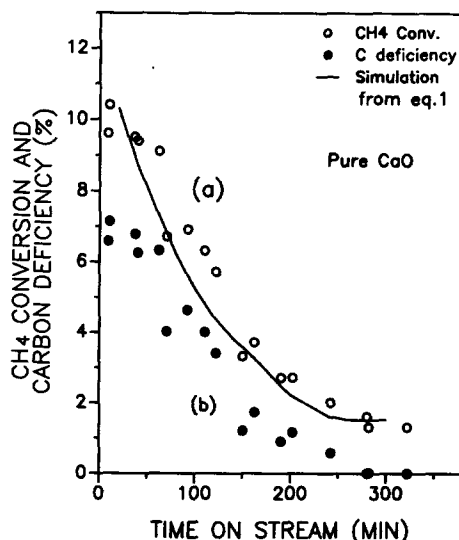
<sup>a</sup> Relative to O(1s) = 1.00.

FIG. 1. (a) Conversion of CH<sub>4</sub> and (b) deficiency in carbon mass balance as a function of time on stream from CaO.

promoted CaO catalyst shown in Figs. 1a and 2a. First, all the catalysts deactivated continuously under reaction conditions to a very low activity level. Second, pure calcium oxide itself was an active catalyst toward methane conversion, mostly into combustion products (see below). The absence of a stable reactivity makes it difficult to correlate the kinetic performance of catalysts to their surface composition at a given condition. For this reason the initial reactivity has been chosen when the performances of different catalysts were compared. The primary goals of this study have been (1) to investigate the relationship between sodium promotion and product selectivity and (2) to formulate the mechanism of catalyst deactivation and then to use this information to elucidate the nature of surface centers responsible for methane activation.

#### 3.1. Effects of Sodium Doping on C<sub>2</sub> Selectivity

As shown in Figs. 1a and 2a, a similar CH<sub>4</sub> conversion (around 10% initially) was obtained from a pure and a 0.5-wt%-Na-

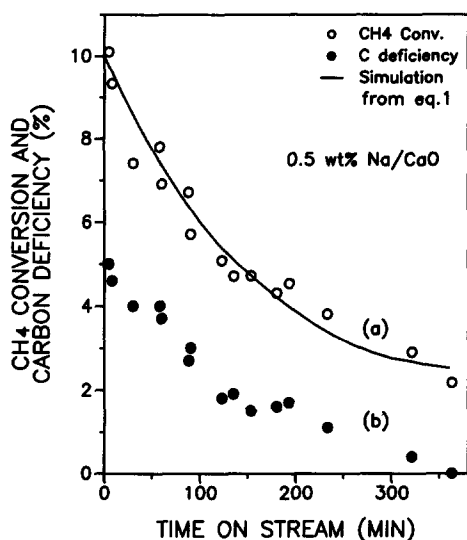


FIG. 2. (a) Conversion of CH<sub>4</sub> and (b) deficiency in carbon mass balance as a function of time on stream from 0.5-wt% Na/CaO.

promoted calcium oxide catalyst. The C<sub>2</sub> selectivity from these catalysts, however, is quite different. Figure 3 displays the initial C<sub>2</sub> selectivity (after less than 10 min on stream) from pure and sodium-promoted CaO catalysts under the standard reaction conditions. It can be seen that the C<sub>2</sub> selectivity increases with sodium loading, from

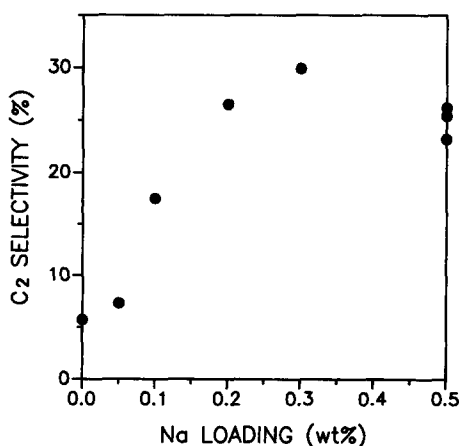


FIG. 3. The initial C<sub>2</sub> selectivity of the catalysts with different Na loadings.

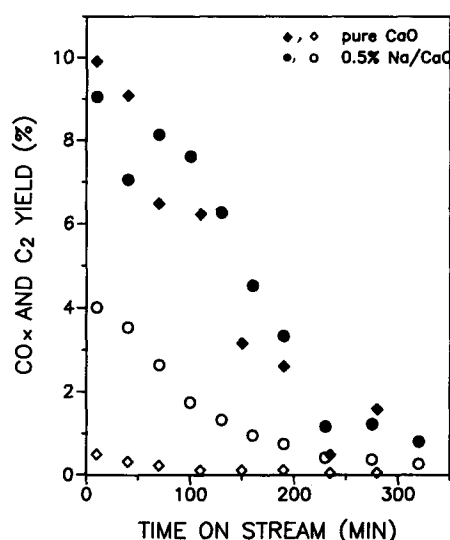


FIG. 4. C<sub>2</sub> and CO<sub>x</sub> yields as a function of time on stream from CaO and 0.5-wt% Na/CaO. Open symbols: C<sub>2</sub> yield; closed symbols: CO<sub>x</sub> yield.

5.7% for a pure CaO catalyst to 26.5% for a 0.2-wt% Na/CaO catalyst, followed by a leveling off above this loading. The leveling off at even higher loading regions was observed in another set of experiments using 2 g of catalysts and a different oxygen pretreatment temperature (550°C); similar C<sub>2</sub> selectivities of 30.9, 39.2, and 33.9 were obtained from 0.5-, 1.0-, and 5.0-wt% catalysts, respectively.

The difference in reactivity between pure and sodium-promoted catalysts can also be illustrated in terms of C<sub>2</sub> and CO<sub>x</sub> (CO plus CO<sub>2</sub>) yields as shown in Fig. 4 for an unpromoted and a 0.5-wt% Na/CaO catalyst pretreated at 550°C with O<sub>2</sub> for 1 hr. The CO<sub>x</sub> yield was calculated by subtracting the C<sub>2</sub> yield from the total CH<sub>4</sub> conversion, instead of using the gas phase product distribution, because part of the combustion products were lost to the solid phase as discussed below. The initial product distribution from these catalysts is summarized in Table 3. Figure 4 demonstrates that pure calcium oxide is essentially a methane combustion catalyst under the reaction conditions with an initial CO<sub>x</sub> yield of 9.9% and an initial C<sub>2</sub>

TABLE 3  
Initial Reactivity of Pure and Sodium-Promoted CaO

Na wt%	Conversion (%)		C <sub>2</sub> Selectivity (%)	Product pressure (Torr)				
	CH <sub>4</sub>	O <sub>2</sub>		CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub> <sup>a</sup>	CO <sup>a</sup>
0	10.4	71.1	4.7	156.8	0.09	0.33	4.56	1.91
0.5	13.0	77.3	30.6	152.2	1.47	2.03	4.59	1.32

<sup>a</sup> CO and CO<sub>2</sub> in the effluent. A portion of these reaction products was lost to the solid phase.

yield of 0.5%, while the sodium-promoted catalyst exhibited a much higher initial C<sub>2</sub> yield, 4.0%. In brief, the results shown above indicate that the presence of sodium on catalyst surfaces is essential for C<sub>2</sub> formation. Similar promotion for C<sub>2</sub> formation by sodium doping on CaO catalysts has been reported in the literature (3, 5).

### 3.2. Catalyst Deactivation

Both pure and sodium-promoted catalysts experienced a rapid deactivation in CH<sub>4</sub> conversion under reaction conditions. As shown in Figs. 1a and 2a, CH<sub>4</sub> conversion decreased over a period of 300 min on stream from 10 to 2% for a pure CaO catalyst and 10 to 3% for a 0.5-wt% Na/CaO catalyst. Among all possible deactivation mechanisms, a change in the composition of the catalyst surface appeared to be the most relevant. It was observed that the carbon mass balance in this period was always less than 100% for both catalysts, with the largest deficiency at the beginning (Figs. 1b and 2b), indicative of a loss of gas phase carbon-containing species to the solid phase. The uptake of the gas phase species by solid surfaces may lead to the catalyst deactivation. This assumption and the gas phase reagent involved in the solid-gas phase reaction were investigated by the following kinetic experiment. The reactivity of a 5-wt% Na/CaO catalyst (2 g) was measured with and without pretreatment by CO<sub>2</sub>, a reaction product. The catalyst pretreated with CO<sub>2</sub> at 650°C exhibited a very low initial activity toward CH<sub>4</sub> conversion

(<2.5%), while the initial CH<sub>4</sub> conversion over the same catalyst without CO<sub>2</sub> pretreatment was 14%. This indicates that reaction between the catalyst surface and gaseous CO<sub>2</sub> is likely to be the reason for catalyst deactivation. The following quantitative simulation provides further support for this assumption.

If the deactivation were due to the reaction between gas phase CO<sub>2</sub> and solid phase, one would expect that the decrease in catalyst activity (i.e., CH<sub>4</sub> conversion) would correspond to the total carbon uptake by the solid phase. That is,

$$\text{Activity at time } t = \text{Initial activity} - A \times \text{Total carbon uptake at } t \quad (1)$$

where  $A$  is a proportionality constant and can be obtained by data regression. The total carbon uptake at a given time can be estimated by integrating the carbon-deficient curves shown in Figs. 1b and 2b from zero to that time, because these curves represent the rate of carbon uptake by the catalyst surface. The simulated results from Eq. (1) are displayed by the solid lines in Figs. 1 and 2 and fit the experimental data very well.

In the above discussion the change in surface area, one of the common causes for catalyst deactivation, has been excluded. In fact, a decrease in surface area was observed for both pure and 0.5-wt% catalysts upon reaction (15.5 to 1.7 m<sup>2</sup>/g for the pure CaO catalyst and 3.3 to 1.5 m<sup>2</sup>/g for the 0.5-wt% Na/CaO catalyst, measured with the Ammco BET apparatus). This effect of sur-

face area change was ignored because little correlation between surface area and reactivity was observed. First, the measured decrease in surface area under reaction conditions is not consistent with the measured decrease in activity; the activity of both promoted and unpromoted catalysts decreased by a factor 5 while the decrease in surface area of CaO was nine-fold and that of Na/CaO twofold. Second, the activity of a catalyst could be regenerated without recovering the surface area. One gram of pure CaO catalyst, pretreated with O<sub>2</sub> at 750°C for 60 min, was operated under the reaction conditions for 170 min to cause a decrease in CH<sub>4</sub> conversion from 13.8 to 1.6% over this period. The catalyst activity was restored to produce a 8.9% CH<sub>4</sub> conversion after treatment with O<sub>2</sub> at 750°C for 60 min. (Regeneration of the CaO catalyst by O<sub>2</sub> treatment is likely due to the conversion of surface calcium carbonate back to calcium oxide.) The surface area of the CaO sample after the second O<sub>2</sub> treatment was the same as that of a deactivated CaO sample (both are 1.6 m<sup>2</sup>/g). These results suggest that a change in catalyst surface area is not the decisive factor in the catalyst deactivation for this system. The lack of a correlation between surface area and reactivity could be general for metal oxide catalysts, because not every accessible atom or ion pair on the surface of such catalysts is necessarily an active center or part of an active ensemble. Rather, active centers on oxide catalysts have often been related to defective structures. The number of active centers on an oxide catalyst need not parallel the surface area.

The surface compositions of pure CaO and CaO promoted with 0.5-wt% Na before and after reaction were characterized by XPS. The XPS spectra in the C(1s) and O(1s) regions from a pure CaO sample after treatment in the VG high pressure cell in O<sub>2</sub> at 640°C for 120 min (similar to the conditions used in the kinetic experiments) are displayed in Fig. 5a. The catalyst exhibited a large O(1s) peak at 528.5 eV with a small

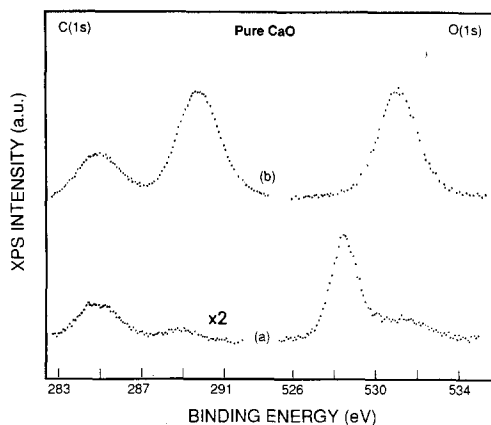


FIG. 5. C(1s) and O(1s) spectra from a CaO catalyst. (a) Treated with O<sub>2</sub> at 640°C for 120 min. (b) Catalyst in (a) treated under reaction conditions for 80 min.

shoulder at the high binding energy side of this peak and two small C(1s) peaks at 284.9 (residual carbon) and 288.9 eV. The calcium-to-oxygen ratio of this surface was found to be near unity; therefore, the major O(1s) peak at 528.5 eV was assigned to calcium oxide. (This peak is 0.9 eV below the reported O(1s) binding energy for CaO (Table 1) for uncertain reasons.) The C(1s) peak at 288.9 eV and the O(1s) shoulder may be attributed to a very small amount of carbonate and hydroxide on the surface. These results indicate that the catalyst surface essentially consisted of calcium oxide prior to reaction. After the sample was treated in the high pressure cell under reaction conditions for 80 min, the major O(1s) peak shifted from the oxide position (528.5 eV) to the carbonate position (531.0 eV) and the carbonate carbon peak at 289.6 eV increased substantially (see Fig. 5b). Quantitative calculation also reveals that the ratio of oxygen to carbonate carbon on the catalyst surface is 3:1, a stoichiometry corresponding to CaCO<sub>3</sub>. These XPS results lead to the conclusion that the catalyst surface was converted from calcium oxide into calcium carbonate under reaction conditions.

The interpretation of XPS spectra from the 0.5-wt% Na/CaO catalyst is less straight-

forward than that of those from the pure CaO catalyst because of interference between the O(1s) and C(1s) peaks from surface sodium and calcium species. The O(1s) and C(1s) binding energies of surface sodium species such as carbonate and oxide are similar to those of the corresponding calcium species (Table 1). It is impractical to decompose these peaks into their sodium and calcium components from the corresponding Ca(2s) and Na(1s) peak area and atomic sensitivity factors, because of the uncertainty introduced by the low sodium concentration on the surface of the 0.5-wt% Na/CaO catalyst (less than 0.06 in mole fraction after O<sub>2</sub> pretreatment or after reaction as estimated from peak area) and the similar metal peak binding energies of sodium or calcium oxides and carbonates. Plausible active sites such as O<sup>-</sup> and O<sub>2</sub><sup>2-</sup> radicals may not exhibit distinguishable O(1s) peaks either, because the reported values, 1.5 to 3.0 eV higher than the oxide peak (7, 10, 14), fall in the binding energy region of the carbonate O(1s) peak. However, total surface oxide and carbonate can be characterized from the well-resolved and dominating O(1s) and C(1s) peaks. The change between these two states under reaction conditions can be detected directly by XPS from the 0.5-wt% Na/CaO catalyst.

The change in O(1s) and C(1s) spectra from the 0.5-wt% Na/CaO sample is similar to that of the pure CaO sample. As shown in Fig. 6, upon treatment in O<sub>2</sub> at 640°C for 150 min, the catalyst exhibited an O(1s) peak at 528.1 eV with a shoulder at its high binding energy side and two small C(1s) peaks at 284.9 (residual carbon) and 289.1 eV, indicating that the catalyst surface consisted mainly of oxide and a small amount of carbonate, hydroxide, and/or oxygen radical centers. After the catalyst was treated in the reactant stream at 640°C for a short time (25 min), the oxide O(1s) peak at 528.1 eV was partly converted to the carbonate O(1s) peak at 531.0 eV, accompanied by the appearance of the carbonate C(1s) peak at 289.5 eV. Longer treatment under reaction

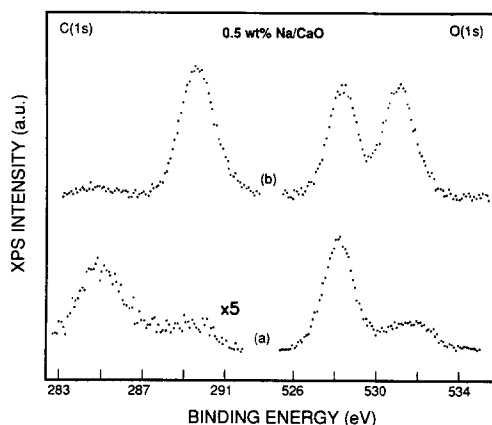


Fig. 6. C(1s) and O(1s) spectra from a 0.5-wt% Na/CaO catalyst. (a) Treated with O<sub>2</sub> at 640°C for 150 min. (b) Catalyst in (a) treated under reaction conditions for 25 min.

conditions in separate experiments brought about the complete conversion of the oxide O(1s) peak into the carbonate O(1s) peak. The ratio of C(1s) and O(1s) peaks formed upon reaction from several samples with different extents of oxide-to-carbonate conversion was always found to be 1:3. These results indicate that surface oxide on the sodium-promoted catalyst was converted into surface carbonate under reaction conditions. The Na(1s) peak at 1071.4 eV did not show a significant shift after reaction, and no systematic changes in surface sodium concentration were observed before and after reaction.

#### 4. DISCUSSION

From the foregoing discussion of the kinetic and XPS results it has become clear that the calcium oxide on both pure and Na-promoted CaO catalysts was converted into calcium carbonate through the reaction with gas phase CO<sub>2</sub> under reaction conditions. Clearly, the disappearance of calcium oxide on the surface of the pure CaO catalyst is responsible for the deactivation of this catalyst. In order to understand the deactivation of the 0.5-wt% Na/CaO catalyst, recall that the mole fraction of sodium on the 0.5-wt%

Na/CaO catalyst surface was less than 0.06. Thus one may suppose that this catalyst consists of promoted and unpromoted CaO phases. While the unpromoted phase acted just as the pure CaO catalyst for methane combustion, the promoted phase was responsible for C<sub>2</sub> formation. The conversion of CaO into CaCO<sub>3</sub> in the unpromoted phase must account for the decrease in CO and CO<sub>2</sub> production from the 0.5-wt% Na/CaO catalyst with time on stream. The remaining question here is how the promoted phase deactivated. One definite change in this phase is the conversion of CaO into CaCO<sub>3</sub> under reaction conditions as shown by XPS. What cannot be determined is the form of surface sodium before and after reaction. Although one may always argue that a change in the form of sodium on the surface could be responsible for the deactivation toward C<sub>2</sub> formation, there are strong indications that the conversion of CaO into CaCO<sub>3</sub> in the promoted phase is the primary cause. If a change in the form of surface sodium species was primarily responsible for the deactivation in C<sub>2</sub> yield, one would expect different trends in C<sub>2</sub> and CO<sub>x</sub> deactivation and a sodium-loading dependence. It can be seen from Fig. 4 that the deactivation in C<sub>2</sub> yield was parallel to the deactivation in CO<sub>x</sub> yield for the 0.5-wt% Na/CaO catalyst. This parallel deactivation was also observed from catalyst with different sodium loadings. The assignment of the deactivation toward C<sub>2</sub> formation of the promoted phase to the conversion of CaO into CaCO<sub>3</sub> also agrees with the proposed models for the active site. As described previously, in the model proposed by Lunsford and co-workers (1-4), an oxide lattice is necessary to form the O<sup>-</sup> centers responsible for CH<sub>4</sub> activation. The models based on surface basicity (5) and morphological defects (6) also require the presence of oxide substrates.

Although sodium doping improved C<sub>2</sub> production, as shown in Figs. 3 and 4, additional sodium above 0.2 wt% had no significant effect on C<sub>2</sub> formation; the C<sub>2</sub> selectivity became approximately constant above

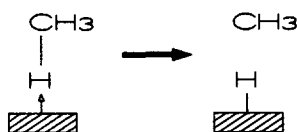
this loading (Fig. 3). A similar result has been observed from Li/MgO catalysts reported previously (7). In the latter case, the leveling off of the C<sub>2</sub> selectivity above a lithium loading level has been attributed to a similar surface composition for the catalysts with lithium loadings above that level. Although this assumption was supported indirectly by O(1s) and C(1s) XPS spectra, the concentration of surface lithium could not be measured in that case because of the low sensitivity of lithium signals and the interference from a magnesium peak. Since sodium has a strong and distinctive Na(1s) XPS emission at ca. 1070 eV, an attempt has been made in the current study to measure the surface sodium composition of catalysts with different sodium loadings by XPS. Surfaces of a 0.5- and a 5-wt%-Na-promoted CaO catalyst were analyzed by XPS after the samples had been treated with O<sub>2</sub> at 640°C in the VG high pressure cell; the surface after this treatment was considered to be most closely related to the initial reactivity of the catalyst. It was observed that the surfaces of these catalysts were composed mainly of calcium oxide and the total sodium mole fraction was 0.04 to 0.11 for the 5-wt% catalyst and 0.02 to 0.06 for the 0.5-wt% catalyst, indicative of a higher sodium concentration on the 5-wt% Na/CaO catalyst. This appears to contradict the assumption of a similar surface composition of catalysts which show similar reactivity. However, since the nature of the surface sodium species could not be determined for the reason discussed above, one cannot be certain what fraction of the sodium on the surface of the 5-wt% catalyst was involved in the active phase and what fraction may have been just inert species. In other words, the surface concentrations of active species in these catalysts might be similar to each other despite the difference in total sodium concentrations.

The change in C<sub>2</sub> selectivity between pure and sodium-promoted CaO phases may be explained by different mechanisms of C-H bond activation in a methane molecule. The

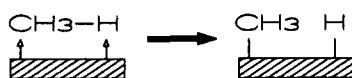


proposition given below is based on the assumption that methyl groups on an oxide surface undergo facile reaction with lattice or adsorbed oxygen to form methoxy. Such a surface methoxy must certainly proceed to form carbon oxides with nearly unit probability on the basis of the well-known chemistry of surface methoxy established by extensive studies of methanol decomposition. In this view, gas phase methyl radicals are the essential intermediate to coupling products. Therefore, any mechanism of C-H activation which produces *surface-bonded methyl* leads to carbon oxides and only mechanisms which produce *free radicals* lead to coupling.

Two classes of C-H bond activation mechanisms can be envisioned, namely, those that proceed by abstraction and those that proceed by insertion.



**Abstraction**



**Insertion**

An abstraction mechanism produces gas phase methyl radicals directly and thus should be the favored route for coupling. Insertion leads to surface-bonded methyl and hence to nonselective, carbon oxide products.

In the case of the pure CaO phase, the C-H bond would be activated by an insertion mechanism. Although no reports have been found about adsorption of  $\text{CH}_4$  on alkaline earth metal oxide surfaces to form methyl groups, heterolytic dissociation of alkenes and alkynes on these surfaces has been well documented (15-17). H-D exchange between  $\text{CH}_4$  and  $\text{D}_2$  has also been reported over alkaline earth metal oxides (16). Note that this mechanism requires two surface sites for dissociated species from a molecule. The basic (oxygen anion) and

acidic (metal cation) pairs on alkaline earth metal oxides are well known for accommodating heterolytically dissociated species (15-17).

In contrast, C-H bond breaking of a methane molecule may proceed through an abstraction mechanism on the sodium-promoted CaO phase. This mechanism has been proposed by Lunsford and co-workers (2); that is, a methane molecule reacts with a surface radical site ( $\text{O}^-$ ) to form a surface H species and a gas phase methyl radical. Note that this reaction may be viewed as a radical transfer from surface to gas phase so that the number of unpaired electrons remains constant. Gas phase methyl formation by a surface with no unpaired electrons must produce two radicals,  $\cdot\text{CH}_3$  and a surface radical, and the latter must undergo recombination to complete the catalytic cycle. Gas phase methyl radicals have been detected under methane oxidative coupling conditions (2), and the combination of methyl radicals in the gas phase to form  $\text{C}_2$  products is a well-established reaction. Note also that a single site is sufficient to generate a methyl radical in this mechanism, as opposed to the pair of sites required by the insertion mechanism. It may not just be a coincidence that most of the active sites for methane oxidative coupling reported in the literature have been single sites such as surface  $\text{O}^-$  and  $\text{O}_2^-$  radicals (2, 18).

Mention that the deactivation behavior described above is subject to the reaction conditions used in this study ( $640^\circ\text{C}$ ,  $\text{CH}_4:\text{O}_2 = 2:1$ ) has to be made. Different results have been observed under other conditions. For instance, a deactivated 0.5-wt% Na/CaO catalyst (3.2% in  $\text{CH}_4$  conversion and 7.9% in  $\text{C}_2$  selectivity) became active again at high temperatures (e.g., 20.5% in  $\text{CH}_4$  conversion and 30.9% in  $\text{C}_2$  selectivity at  $740^\circ\text{C}$ ). When the reaction temperature was decreased back to  $640^\circ\text{C}$ , the catalyst exhibited a reactivity similar to that prior to the high temperature experiment (5.2% in conversion, 10.9% in  $\text{C}_2$  selectivity). A sec-

ond case is for a reaction at 700°C. A 0.5-wt% Na/CaO catalyst operated at this temperature exhibited a 16% CH<sub>4</sub> conversion after 9 hr on stream, instead of being deactivated completely. The CH<sub>4</sub>-to-O<sub>2</sub> ratio in the reaction feed also proved to be a factor in deactivation pattern. The effect of reaction conditions upon surface composition of the catalyst is under investigation. Different deactivation behaviors under different reaction conditions can be understood from the thermodynamic equilibrium between CaO and CaCO<sub>3</sub>, i.e.,



The equilibrium concentration depends on both temperature and CO<sub>2</sub> partial pressure. A recent work by Suzuki *et al.* (19) has clearly demonstrated how this equilibrium shifts with different content of CO<sub>2</sub> in the reaction feed and how this shift affects the CH<sub>4</sub> conversion. Finally, for the different deactivation behaviors at high temperature (e.g., >700°C), a different mechanism for oxidative coupling, which does not require the presence of CaO, may become operative. As proposed by Lunsford and co-workers (20), the active sites for methane activation on alkaline metal-promoted catalysts at temperatures above 720°C may be alkaline metal species, e.g., peroxide intermediates, instead of O<sup>-</sup>-type centers. Otsuka has also suggested the role of alkaline or alkaline earth metal peroxides in methane activation (18).

The foregoing discussion leads to the conclusion that the high C<sub>2</sub> selectivity from Na-doped CaO catalysts is due to the selective sites made up of sodium species associated with CaO lattices. However, one could propose a different explanation. That is, CH<sub>4</sub> was activated by the pure CaO phase, and it is the migration of the activated methane to other surface-oxidizing sites that produced combustion products. Sodium doping on CaO could poison these oxidizing sites, leading to higher C<sub>2</sub> selectivity. Although similar CH<sub>4</sub> conversions from a pure CaO and a 0.5-wt% Na/CaO catalyst shown in

Figs. 1 and 2 seem to agree with this explanation, this is purely a coincidence. Other experiments, e.g., the results in Table 3, have exhibited different CH<sub>4</sub> conversions between pure CaO and Na/CaO catalysts. Furthermore, as indicated above, the CaO and Na/CaO catalysts corresponding to the results in Figs. 1 and 2 had initial surface areas of 15.5 and 3.3 m<sup>2</sup>/g, respectively. If the pure CaO phase were responsible for CH<sub>4</sub> activation, one would expect that the initial CH<sub>4</sub> conversion from the pure CaO sample would be four times that from the 0.5-wt% Na/CaO sample, contrary to the experimental observation.

## 5. CONCLUSIONS

Both pure and sodium-promoted calcium oxide catalysts were active for methane activation. While the pure CaO catalyst produced essentially CO<sub>2</sub> and CO, its C<sub>2</sub> selectivity could be improved by sodium doping. Calcium oxide was found to be an active component in both pure and promoted catalysts. Conversion of calcium oxide to calcium carbonate under reaction conditions led to catalyst deactivation. The fact that the presence of both sodium and calcium oxide is necessary for C<sub>2</sub> formation suggests that the active phase in Na/CaO catalysts toward C<sub>2</sub> formation consists of sodium species associated with calcium oxide. The difference in the C<sub>2</sub> selectivity between pure and promoted catalysts may be due to different methane activation mechanisms, i.e., insertion vs abstraction, over these catalysts.

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