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# Oxidative Coupling of Methane over Calcium Oxide and Gadolinium Oxide Promoted with Sodium Pyrophosphate

RANJANI V. SIRIWARDANE

*U.S. Department of Energy, Morgantown Energy Technology Center, P.O. Box 880, Morgantown, West Virginia 26507-0880*

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Calcium oxide and gadolinium oxide, both promoted with sodium pyrophosphate, were found to be active and selective catalysts for the partial oxidation of methane to ethane and ethylene in the presence of molecular oxygen. Yields of $C_2$ hydrocarbons as high as 18 to 19% were obtained over $Na_4P_2O_7/CaO$, while yields of 17 to 18% were obtained over $Na_4P_2O_7/Gd_2O_3$ at 1101 K. For $Na_4P_2O_7/CaO$ there was no appreciable change in either $C_2$ yield or total conversion of $CH_4$ during the 26-h testing period at 1101 K, while there was a small decrease in the $C_2$ yield over $Na_4P_2O_7/Gd_2O_3$ after 20 h of reaction. Elemental composition of the surface of the catalysts analyzed by Auger electron spectroscopy correlated well with catalytic performance data. Analysis of the elemental composition obtained by Auger electron spectroscopy of the catalysts (1101 K) indicated that a larger portion of sodium was retained on the surface after reaction on catalysts containing $Na_4P_2O_7$ than on catalysts containing $Na_2CO_3$. The stability at 1101 K of the catalysts containing $Na_4P_2O_7$ was also greater than that of the catalysts containing $Na_2CO_3$. Phosphorus on the surface of $Na_4P_2O_7/CaO$ was found to stabilize the sodium on the surface without being consumed during the reaction. Changes in surface morphology after the reaction were also observed by scanning electron microscopy. X-ray photoelectron spectroscopic (XPS) data indicated that oxygen, sodium, and phosphorus were in similar chemical states on $Na_4P_2O_7/CaO$ and $Na_4P_2O_7/Gd_2O_3$. Carbide formation was observed on the catalysts after exposure to methane.

## INTRODUCTION

Methane is the major component of natural gas and is used primarily as fuel. Transport of natural gas has been a problem in the exploitation of some natural gas resources. It would be extremely valuable to be able to convert methane to more readily manageable or transportable products. However, the high molecular stability of methane makes it difficult to convert into other useful chemicals. Reasonable progress has been made in the past in catalytic oxidative coupling of methane to form higher hydrocarbons which could be used as gasoline precursors. Several oxide catalysts *(1–10)* promoted with alkali metals have shown to be promising catalysts for this process.

The objective of this work is to obtain further information on the catalytic oxidative coupling of methane. The results of both reactor studies and surface characterization studies on two new promising catalysts, namely, calcium oxide and gadolinium oxide, both promoted with sodium pyrophosphate, which could be used for selective conversion of methane, are reported in the present study.

## EXPERIMENTAL

### *Reactor Studies*

CaO was prepared by decomposition of calcium acetate (Aldrich) at 1123 K for 16 to 19 h. Promoted calcium oxide was prepared by adding calcium oxide and sodium pyrophosphate (Alfa) to deionized water and slowly evaporating water while stirring. The resulting thick solid paste was

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heated in an oven at 773 K for 16 h followed by 2 h heating at 973 K. Gadolinium oxide was prepared by heating gadolinium nitrate (Aldrich) in an oven at 1123 K for 16 to 18 h. The resulting gadolinium oxide was promoted with sodium pyrophosphate using a procedure similar to that for calcium oxide. Oxides promoted with sodium carbonate (Fisher) were prepared using a similar procedure that was used for promotion of the catalysts with sodium pyrophosphate.

Each catalyst of 28 to 48 mesh and 0.25 g was placed in a high-purity quartz tube (length = 23.3 cm, diameter = 4.5 mm, heated zone length = 9 cm). Ultrahigh-purity (99.999%) helium, grade zero oxygen gas (99.8%), and methane (99.99%) were obtained from Matheson. The catalytic experiments were carried out in a fixed-bed reactor operated at 1 atm. Reacting gas mixtures of methane and oxygen diluted with helium to achieve a total pressure of 1 atm were introduced after the catalyst was heated to the desired temperature. The gaseous products were analyzed with two gas chromatograph columns (Porapak Q and molecular sieve) which were connected to a thermal conductivity detector. The mole ratios that are used in the discussion of the results in the present paper are the moles of sodium promoter per mole of oxide. The term "yield" used in this paper was obtained by multiplying the selectivity for each carbon-containing product and the total $CH_4$ conversion (based on mole percentages). The "percentage" of $C_2H_4$, $C_2H_6$, CO, and $CO_2$ shown in the graphs is the percentage "yield" of each compound.

### *Surface Characterization*

The surface area of the catalysts was measured by a volumetric method using nitrogen and krypton gases. Auger electron spectroscopic analysis and scanning Auger mapping analysis of elements on the surface were performed using a Perkin–Elmer SAM-590 system. Total elemental analysis was performed by atomic absorption spectroscopy. Surface acidity tests were performed by the indicator method (*11*). Indicators alizarin (Fisher) and *o*-nitrophenol (Fisher) were dissolved in nonpolar solvents such as toluene and cyclohexane. The solid samples were added to the indicator solutions, and color changes were observed on the surface of the solid. X-ray photoelectron spectra were recorded with a Cylindrical Mirror Analyzer and a 15-kV X-ray source (Physical Electronics Division of Perkin–Elmer). Charge correction of the XPS data was accomplished by assuming that the binding energy of the C 1*s* peak was at 284.6 eV.

## RESULTS

### *Reactor Studies*

The optimum yields of $C_2$ compounds on both $Na_4P_2O_7/CaO$ and $Na_4P_2O_7/Gd_2O_3$ were obtained by varying reaction conditions such as sodium concentration, temperature, and ratio of methane-to-oxygen gas compositions. The results of these studies are discussed in the following sections. $C_2$ yields of 18 to 19% were obtained on $0.1Na_4P_2O_7/CaO$ while 17 to 18% yields were obtained $0.5Na_4P_2O_7/Gd_2O_3$, at 1101 K and a methane-to-oxygen ratio of 2. These $C_2$ yields were comparable to the highest $C_2$ yields reported in the literature on the other active catalysts (*2, 7, 10*).

The $C_2$ yield of 18 to 19% on $0.1\ Na_4P_2O_7/CaO$ did not vary during the testing period of 26 h. These results are also discussed below.

*Variation in catalytic performance with time.* The change in catalytic performance during the reaction at 1101 K was examined using CaO, $0.1Na_4P_2O_7/CaO$, and $0.1Na_2CO_3/CaO$, and the results are shown in Fig. 1. Pure CaO produced a low $C_2$ yield (the product of the total $CH_4$ conversion and selectivity for $C_2$ compounds), and this $C_2$ yield did not decrease during the 20-h period of testing. There was a substantial increase in the $C_2$ yield for both $0.1Na_2CO_3/CaO$ and $0.1Na_4P_2O_7/CaO$ compared to that for the pure CaO. The initial $C_2$ yields

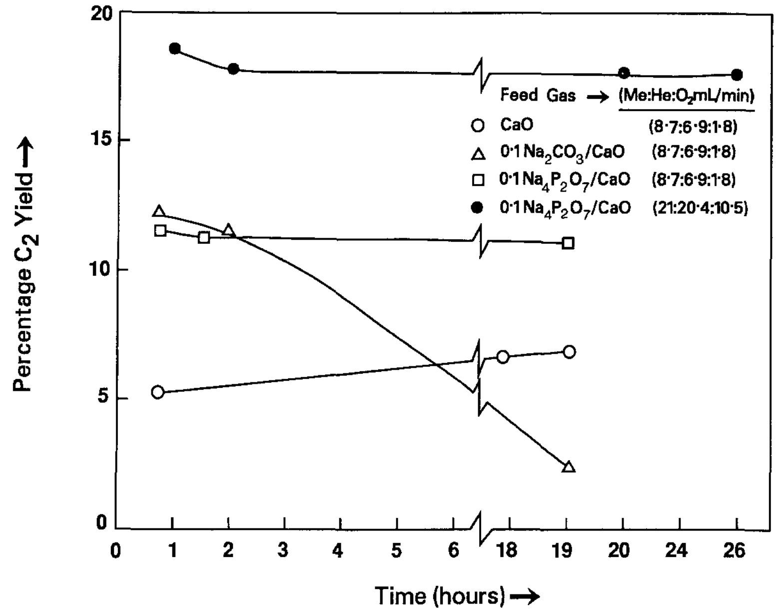

FIG. 1. $C_2$ yield of catalysts containing CaO as a function of time at 1101 K.

(12%) for both $0.1Na_2CO_3/CaO$ and $0.1Na_4P_2O_7/CaO$ were similar, but over 19 h, there was a drastic decrease in the $C_2$ yield over $0.1Na_2CO_3/CaO$. It is interesting that there was no substantial decrease in the $C_2$ yield even after 26 h over $0.1Na_4P_2O_7/CaO$ under both reaction conditions with methane-to-oxygen ratios (based on partial pressures) of 2 : 1 and 5 : 1 as shown in Fig. 1. The product distribution for $C_2H_4$, $C_2H_6$, $CO_2$, and CO was also not changed during 26 h on $0.1Na_4P_2O_7/CaO$.

The results were different for $Gd_2O_3$ promoted with $Na_4P_2O_7$ as shown in Fig. 2. There was no significant change in $C_2$ yield for $0.5Na_4P_2O_7/Gd_2O_3$ during 21 h of reaction when the methane-to-oxygen ratio was 5. However, when the methane-to-oxygen ratio was 2 there was about a 13% decrease from the original $C_2$ yield during the period from 4 to 20 h, but it remained constant after 20 h. However, with $Na_2CO_3/Gd_2O_3$, there was a decrease in the $C_2$ yield of 25% during the period 2 to 23 h, even when the methane-to-oxygen ratio was 5 which was more than that observed with $Na_4P_2O_7/Gd_2O_3$. This was consistent with the observation that $Na_4P_2O_7$ contributed to better stability of the CaO-promoted catalyst compared to $Na_2CO_3$.

*Effect of the sodium concentration.* Variation in catalytic performance at 1101 K as a function of $Na_4P_2O_7$ content on CaO is shown in Fig. 3. The flow rates of methane, oxygen, and helium were 21, 10.5, and 20.4 ml/min, respectively. Under these conditions, the empty reactor at 1101 K produced 5% $C_2$ yield with 46% selectivity. Both pure CaO and pure $Na_4P_2O_7$ produced $C_2$ yields higher than the empty reactor. Addition of $Na_4P_2O_7$ to CaO produced higher $C_2$ yields compared with those corresponding to both pure CaO and pure $Na_4P_2O_7$. The maximum $C_2$ yield was obtained when the $Na_4P_2O_7$ content on CaO was between 0.1 and 0.2 mol. Total conversion of $CH_4$ and $C_2$ selectivity also went through a maximum with increasing $Na_4P_2O_7$ content. Pure $Na_4P_2O_7$ produced very low $CO_2$ and high CO, but the reverse was observed over pure CaO. It is interesting that the addition of $Na_4P_2O_7$ up to 0.2

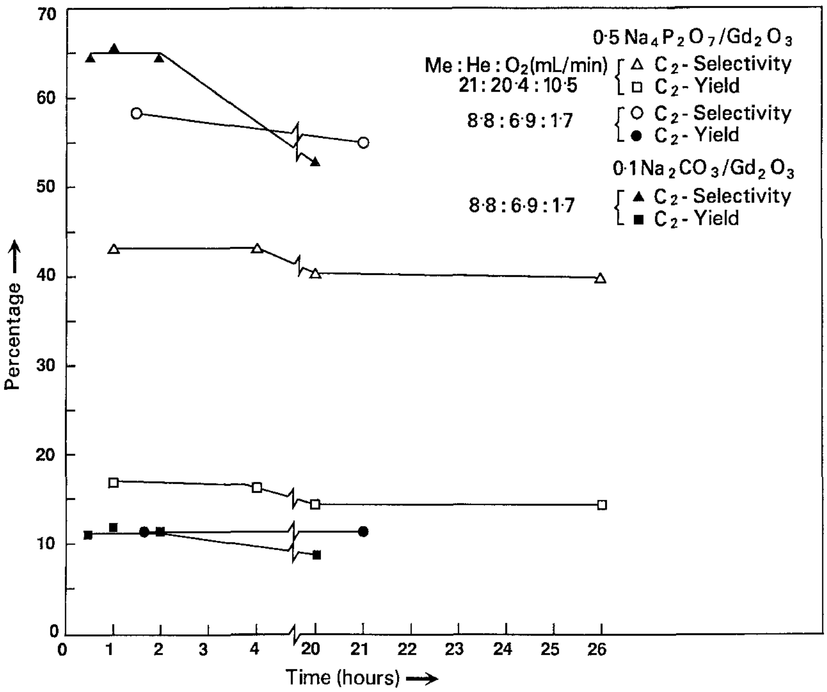

FIG. 2. $C_2$ yield of catalysts containing $Gd_2O_3$ as a function of time at 1101 K.

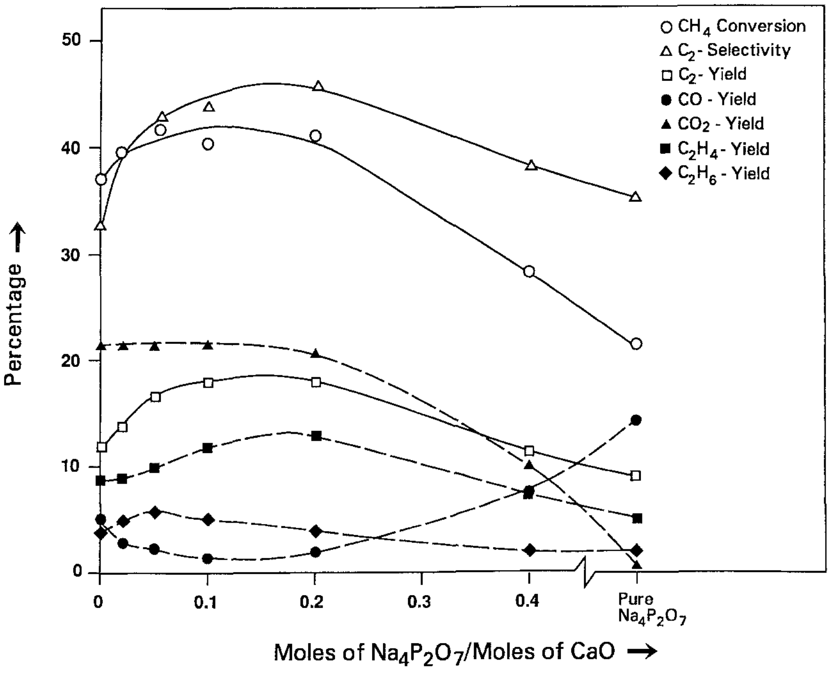

FIG. 3. Effect of sodium concentration on the catalyst $Na_4P_2O_7/CaO$ at 1101 K.

mol to CaO suppressed the formation of both CO and $CO_2$ but increased the formation of $C_2H_4$ and $C_2H_6$ compared to that of both pure CaO and pure $Na_4P_2O_7$. Thus, there was a unique interaction between $Na_4P_2O_7$ and CaO which created sites that produced high $C_2$ yields. However, further increase in $Na_4P_2O_7$ decreased the $C_2$ products and $CO_2$ formation and increased the CO formation which was similar to that of pure $Na_4P_2O_7$.

The effect of $Na_4P_2O_7$ content on catalytic performance on $Gd_2O_3$ is shown in Fig. 4. The behavior was different from what was observed with $Na_4P_2O_7$/CaO. Initially (up to 0.1 mol of $Na_4P_2O_7$), there was a decrease in $C_2$ selectivity, $CH_4$ total conversion, and $C_2$ yield with the addition of $Na_4P_2O_7$ to $Gd_2O_3$. However, all of these parameters increased with further addition of $Na_4P_2O_7$. The maximum $C_2$ yield was observed at 0.5 mol of $Na_4P_2O_7$. As a comparison, when 0.1 mol of $Na_2CO_3$ was added to $Gd_2O_3$, the $C_2$ yield was similar to that of 0.5 mol $Na_4P_2O_7/Gd_2O_3$ even though the catalytic deactivation was drastic for 0.1 $Na_2CO_3/Gd_2O_3$. Thus, a larger amount of $Na_4P_2O_7$ was necessary for $Gd_2O_3$ to obtain a $C_2$ yield similar to that obtained with either 0.1$Na_2CO_3/Gd_2O_3$ or 0.1$Na_4P_2O_7$/CaO.

*Effect of temperature.* Catalytic performance of 0.1$Na_4P_2O_7$/CaO as a function of temperature is shown in Fig. 5. Flow rates of $CH_4$, $O_2$, and He were 21, 10.5, and 20.4 ml/min, respectively. Conversion of $CH_4$, $C_2$ yield, and $C_2$ selectivity increased with increasing temperature up to 1101 K. Previous workers (*9*) observed the maximum catalytic performance with $Na_2CO_3$/CaO ($C_2$ yield of 14 to 15%) at a temperature of 993 K.

The effect of temperature on the catalytic performance of 0.5$Na_4P_2O_7/Gd_2O_3$ is shown in Fig. 6. The results were similar to those observed over 0.1$Na_4P_2O_7$/CaO. Variation of products with temperature was also similar to that of 0.1$Na_4P_2O_7$/CaO. The amounts of the products $CO_2$, $C_2H_4$, and $C_2H_6$ increased with increasing temperature up to 1101 K.

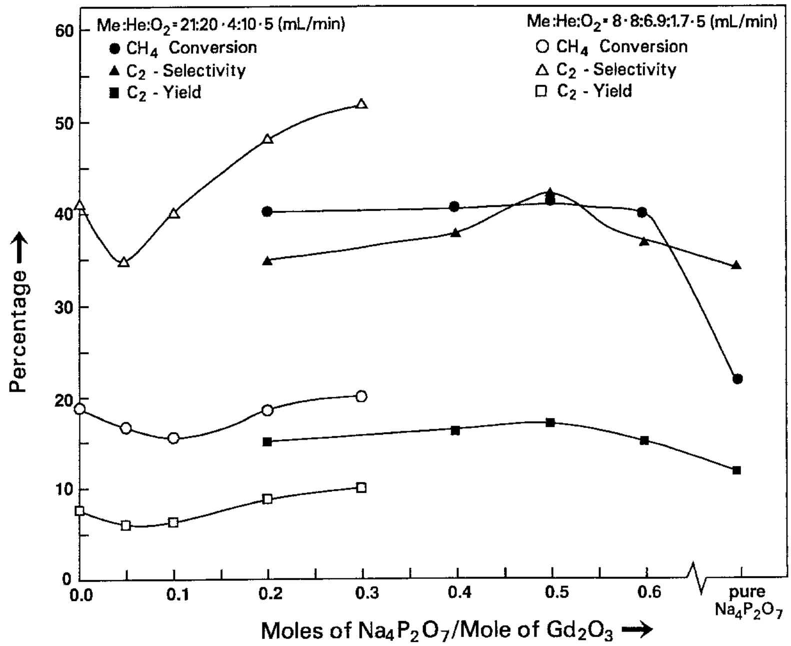

FIG. 4. Effect of sodium concentration on the catalyst $Na_4P_2O_7/Gd_2O_3$ at 1101 K.

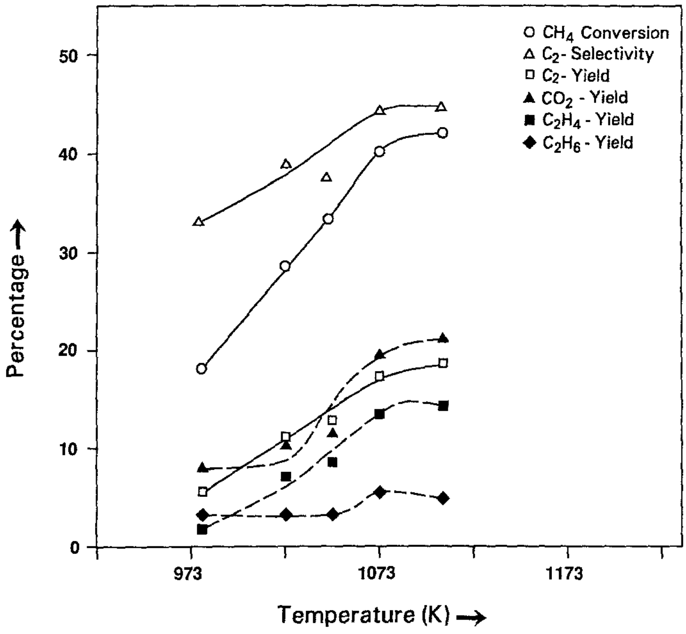

FIG. 5. Effect of temperature on the catalyst $0.1Na_4P_2O_7/CaO$.

*Effect of methane-to-oxygen ratio.* To optimize the reaction conditions to obtain the maximum $C_2$ yield over $0.1Na_4P_2O_7/$CaO, experiments were carried out using reactant mixtures with different methane and oxygen gas compositions (based on the partial pressures). The flow rate of helium was 20.4 ml/min, while total flow rate of methane and oxygen was 31.5 ml/min. Under these flow conditions, the methane-to-oxygen ratio was varied. The results of these experiments are shown in Fig. 7. With increasing methane-to-oxygen ratio, the overall conversion of methane decreased while the selectivity for $C_2$ compounds increased. This decrease in the $CH_4$ conversion was consistent with the drastic decrease in the amount of $CO_2$ formation with increasing methane-to-oxygen ratio. When the $CH_4$-to-$O_2$ ratio was decreased from 5 to 2 (Fig. 7) at a constant total $CH_4$ and $O_2$ pressure, the $CO_2$ formation, $C_2$ products, and CO yields increased while the formation of $C_2H_6$ remained constant. Further decrease in the methane-to-oxygen ratio to 1 resulted in a large increase in $CO_2$, a small increase in CO, and a small decrease in $C_2$ product yields. Thus, the maximum $C_2$ yield of 18 to 19% was ob-

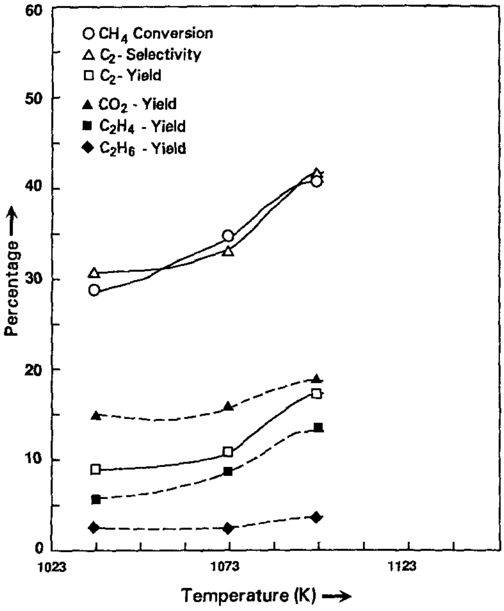

FIG. 6. Effect of temperature on the catalyst $0.1Na_4P_2O_7/Gd_2O_3$.

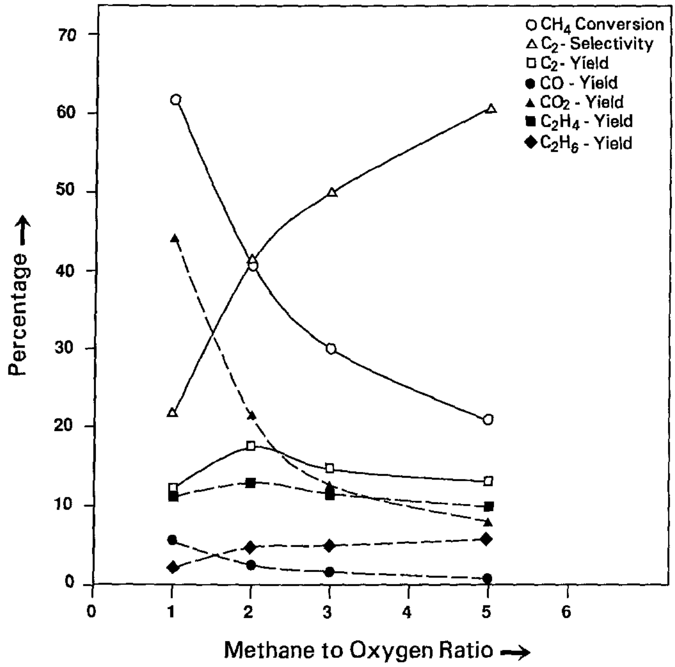

FIG. 7. Effect of methane-to-oxygen ratio on the catalyst $0.1Na_4P_2O_7/CaO$ at 1101 K.

tained over $0.1Na_4P_2O_7/CaO$ when the methane-to-oxygen ratio was 2. The $C_2$ yield over $0.5Na_4P_2O_7/Gd_2O_3$ was 17 to 18% when the methane-to-oxygen ratio was 2. Oxygen conversion at a methane-to-oxygen ratio of 5 was very high (~95%).

### *Surface Characterization*

*Scanning electron microscopy.* Scanning electron photomicrographs of the catalysts containing CaO are shown in Fig. 8. A porous structure with uniformly distributed interconnecting network-type arrangement was observed on pure CaO. This arrangement was changed on unreacted $0.1Na_4P_2O_7/CaO$ in which more round particles and aggregates were observed. A third type of structure was observed on $0.1Na_4P_2O_7/CaO$ after the reaction. The round particles or the aggregates were not observed, but a uniformly distributed structure with sharp edges was more visible on the surface. The surface morphology of unreacted $0.1Na_2CO_3/CaO$ (not shown here) was similar to that of $0.1Na_4P_2O_7/CaO$ before the reaction. However, after the reaction, the $0.1Na_2CO_3/CaO$ surface appeared to have agglomerated round particles and hence the surface morphology was completely different from that of $0.1Na_4P_2O_7/CaO$. Significant changes in surface morphology were not observed on $0.5Na_4P_2O_7/Gd_2O_3$ before or after the reaction.

*Auger electron spectroscopy.* Auger electron spectroscopic (AES) analysis was performed on five different locations on each sample. AES provides elemental analysis of the surface of the sample up to a depth of about 30 Å. Since the catalytic reactions essentially take place on the surface of the sample, it is useful to know the elemental composition on the surface. The results of the elemental analysis by AES on the surfaces of promoted CaO are shown in Table 1. The "average" indicates the average of the elemental ratios at different positions, while "maximum" and "minimum" indicate the maximum and minimum elemental ratios over those positions, respectively. As shown in Table 1, the distribution

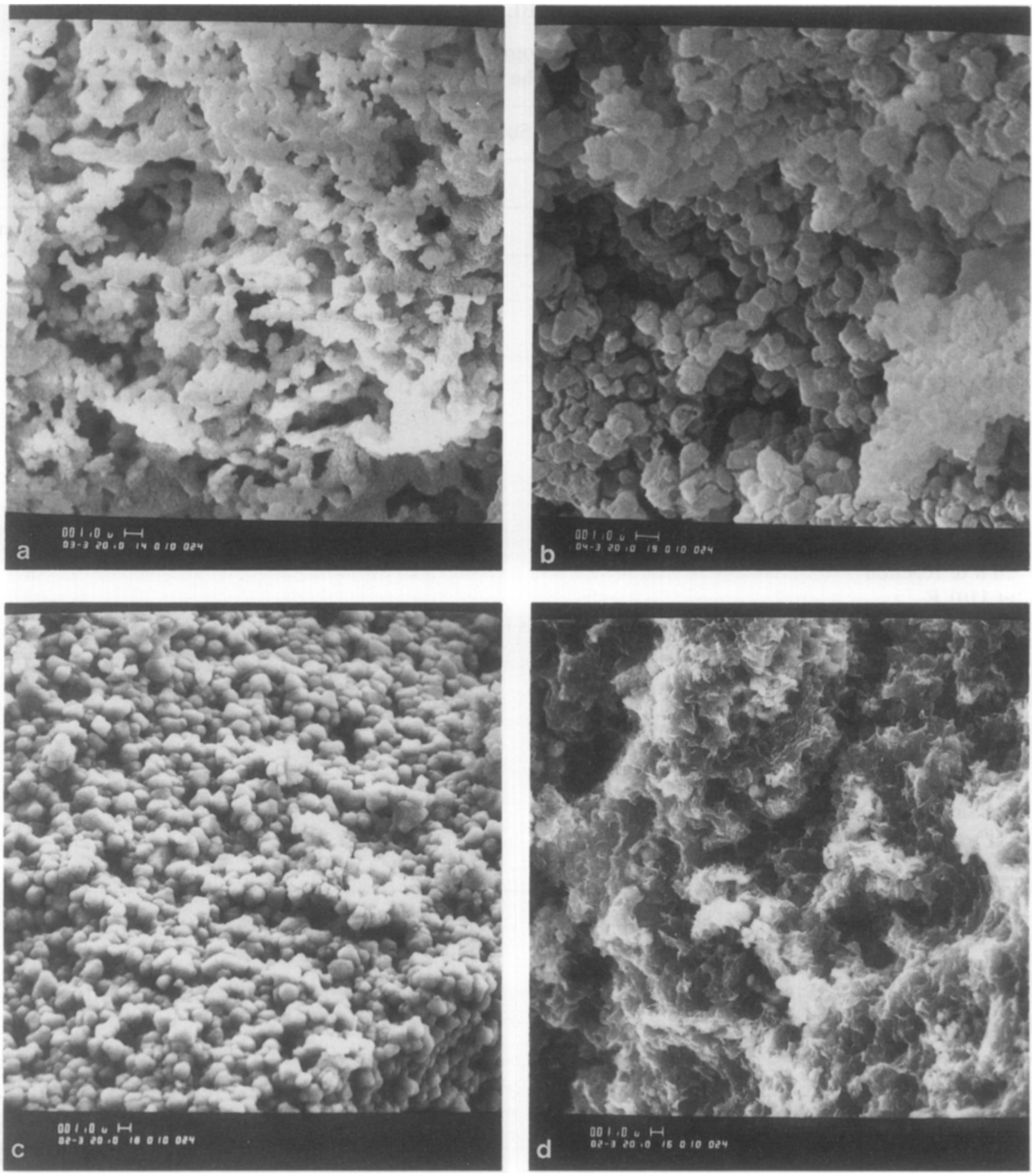

FIG. 8. Scanning electron photomicrographs of CaO containing sodium before and after reaction. (a) CaO, (b) $0.1Na_4P_2O_7/CaO$, (c) $0.1Na_2CO_3/CaO$ after reaction, (d) $0.1Na_4P_2O_7/CaO$ after reaction.

of sodium on the surface of $0.1Na_4P_2O_7/CaO$ was nonuniform. After 26 h of reaction, there was a decrease in the amount of sodium, while there was no significant change in the amount of phosphorus. The decrease in the amount of sodium may have been due to the fact that the sample of $0.1Na_4P_2O_7/CaO$ was kept at a high temperature of 1101 K for 26 h during the reaction. To check this, the sample was heated at 1101 K without the reactants for 26 h. As shown in Table 1, there was no significant change in either sodium or phosphorus on the surface after the sample was kept at

TABLE 1

Elemental Analysis by Auger Electron Spectroscopy (AES) and Total Elemental Analysis by Atomic Absorption Spectroscopy (AAS) of the Surfaces of the Catalysts Containing CaO before and after Reaction

| Sample | Surface elemental analysis (AES) | | | | | |
|---|---|---|---|---|---|---|
| | Na/Ca | | | P/Ca | | |
| | Average | Maximum | Minimum | Average | Maximum | Minimum |
| 1. $0.1Na_4P_2O_7/CaO$ before reaction | 0.29 | 0.51 | 0.17 | 0.06 | 0.09 | 0.03 |
| 2. $0.1Na_4P_2O_7/CaO$ after 26 h reaction at 1101 K | 0.10 | 0.14 | 0.04 | 0.05 | 0.08 | 0.02 |
| 3. $0.1Na_4P_2O_7/CaO$ 26 h at 1101 K (no reactants) | 0.29 | 0.40 | 0.17 | 0.07 | 0.13 | 0.05 |
| 4. $0.1Na_2CO_3/CaO$ before reaction | 0.10 | 0.15 | 0.07 | — | — | — |
| 5. $0.1Na_2CO_3/CaO$ after 20 h of reaction at 1101 K | 0.04 | 0.06 | 0.00 | — | — | — |
| | Total elemental analysis (AAS) Na/Ca | | | | | |
| 1. $0.1Na_4P_2O_7/CaO$ before reaction | 0.12 | | | | | |
| 2. $0.1Na_4P_2O_7/CaO$ after 26 h reaction | 0.06 | | | | | |
| 3. $0.1Na_2CO_3/CaO$ before reaction | 0.08 | | | | | |
| 4. $0.1Na_2CO_3/CaO$ after 20 h reaction | 0.07 | | | | | |

1101 K for 26 h without the reactants. Thus, the loss of sodium could have occurred only in the presence of the reactants. The amount of sodium on $0.1Na_4P_2O_7/CaO$ after 4 h of reaction was also found to have decreased (with Na/Ca = 0.14) compared to that on the original sample. This ratio of Na/Ca after 4 h of reaction was similar to that (Na/Ca = 0.10) on the catalyst after 26 h of reaction.

The amount of sodium on the surface of $0.1Na_2CO_3/CaO$ before the reaction was lower than that of $0.1Na_4P_2O_7/CaO$ before the reaction, but was similar to that of $0.1Na_4P_2O_7/CaO$ after 4 and 26 h of reaction. However, there was a considerable loss in the amount of sodium on the surface of $0.1Na_2CO_3/CaO$ after 20 h of reaction, with certain regions with zero sodium content.

To investigate how the sodium was distributed on the $0.1Na_4P_2O_7/CaO$ before the reaction, scanning Auger mapping analysis was performed (in one of the regions used for AES) on the sample. The photograph of the mapping analysis of sodium on $0.1Na_4P_2O_7/CaO$ is shown in Fig. 9. It was interesting to note that sodium was randomly distributed on the surface.

Results of the AES analysis on promoted $Gd_2O_3$ are shown in Table 2. The distribution of sodium on the surface was nonuniform on $0.5Na_4P_2O_7/Gd_2O_3$ before the reaction and was similar to the observations made on $0.1Na_4P_2O_7/CaO$ before the reaction as shown in Table 1. There was a small

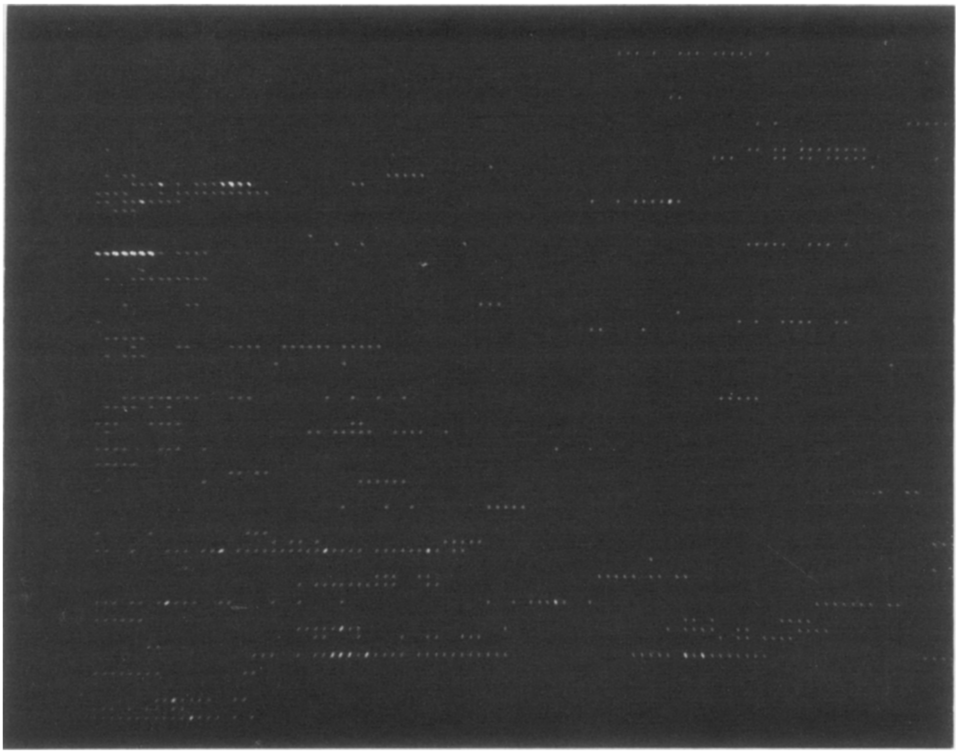

FIG. 9. Scanning Auger mapping analysis of sodium on $0.1Na_4P_2O_7/CaO$ surface before reaction.

decrease in the amount of sodium on the surface of $0.5Na_4P_2O_7/Gd_2O_3$ after the reaction. However, this decrease in sodium was less than what was observed on $0.1Na_4P_2O_7/CaO$. The distribution of sodium on $0.5Na_4P_2O_7/Gd_2O_3$ after the reaction was more uniform compared to that on $0.5Na_4P_2O_7/Gd_2O_3$ before the reaction. It was also interesting to note that $0.5Na_2CO_3/Gd_2O_3$ had an amount of sodium on the surface similar to that on $0.1Na_2CO_3/Gd_2O_3$. However, after the reaction, there was a significant decrease in the amount of sodium on $0.1Na_2CO_3/Gd_2O_3$ surface which was consistent with the observation made on $0.1Na_2CO_3/CaO$. The Auger (AES) peak corresponding to phosphorus overlapped with lower binding energy peaks of gadolinium; thus, it was difficult to detect phosphorus peaks on samples containing $Gd_2O_3$ by AES.

TABLE 2

Elemental Analysis by Auger Electron Spectroscopy of the Surfaces of the Catalysts Containing $Gd_2O_3$ before and after Reaction

| Sample | Na/Gd | | |
|---|---|---|---|
| | Average | Maximum | Minimum |
| 1. $0.5Na_4P_2O_7/Gd_2O_3$ before reaction | 0.32 | 0.59 | 0.04 |
| 2. $0.5Na_4P_2O_7/Gd_2O_3$ after reaction | 0.26 | 0.32 | 0.23 |
| 3. $0.1Na_2CO_3/Gd_2O_3$ before reaction | 0.33 | 0.39 | 0.25 |
| 4. $0.1Na_2CO_3/Gd_2O_3$ after reaction | 0.14 | 0.16 | 0.12 |

*Atomic absorption spectroscopic analysis.* Total elemental analyses of sodium and calcium are also shown in Table 1. The results are entirely different from the surface elemental analyses. The ratio of total Na/Ca was not changed after reaction on $Na_2CO_3/CaO$, while in $Na_4P_2O_7/CaO$ there was a decrease in total Na/Ca after reaction. It is also important to note that the surface Na/Ca ratio is more (about twice) than that in the bulk on the $Na_4P_2O_7/CaO$ before the reaction, indicating that the sodium is distributed mostly near the surface. The total Na/Ca ratio of $0.1Na_4P_2O_7/CaO$ before the reaction was lower than the theoretically expected value of 0.4 (according to the formula). During preparation of the catalyst, all of the sodium may not have deposited on the CaO.

*X-ray photoelectron spectroscopic analysis (XPS).* The XPS system consisted of a separately pumped ($10^{-8}$–$10^{-7}$ Torr; 1 Torr = 133.3 Pa) sample preparation chamber which was equipped with a resistively heated sample probe and a leak valve for gas exposures. The preparation chamber was separated from the analyzing chamber by a gate valve. Catalyst samples were heated in the preparation chamber to 1101 K and were exposed to pure oxygen and methane/oxygen mixture (2 : 1) at 1101 K at a constant pressure for 10 min. Then the gate valve was opened and the sample was transferred to the analyzing chamber for data acquisition at 1101 K. This procedure ensured that there was no rehydroxylation or any other contamination of the samples due to exposure to the atmosphere during the transfer of the samples from reactor to spectrometer. The experimental uncertainty in the binding energy was ±0.5 eV. XPS provides analysis of the surfaces of the samples up to a depth of about 50 Å. The binding energy of elements obtained by XPS can generally be used to differentiate the chemical states of the elements on the surface. The XPS spectrum of the O 1*s* peak of $0.1Na_4P_2O_7/CaO$ at 1101 K is shown in Fig. 10. Only one oxygen peak was observed at 530.9 eV and this peak was not changed after exposure to both oxygen and methane/oxygen (1 : 2) mixtures at 2400 Langmuirs (1 Langmuir = exposure to $10^{-6}$ Torr for 1 s). Similar observations were made with $0.5Na_4P_2O_7/Gd_2O_3$ system. The binding energies of O 1*s* for the different compounds at 1101 K are shown in Table 3. The binding energy of oxygen on both $Na_4P_2O_7/CaO$ and $Na_4P_2O_7/Gd_2O_3$ was similar to that of $Na_4P_2O_7$. The oxygen binding energy of $Na_4P_2O_7/CaO$ was different from that of CaO even though a calcium peak was observed on this catalyst. The higher binding energy of oxygen on $Na_4P_2O_7/CaO$

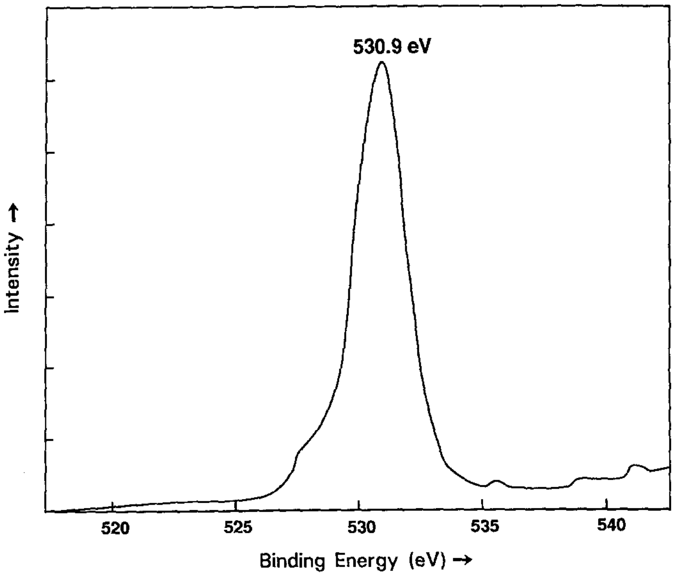

FIG. 10. XPS spectra of O 1*s* peak on $Na_4P_2O_7/CaO$.

TABLE 3

Binding Energy of Oxygen and Phosphorus on $0.1Na_4P_2O_7/CaO$, $0.5Na_4P_2O_7/Gd_2O_3$, and Standard Compounds

| Compound | Binding energy (eV) | |
|---|---|---|
| | O | P |
| $Na_4P_2O_7$ at 1101 K | 531.2 | 132.8 |
| $0.1Na_4P_2O_7/CaO$ at 1101 K | 531.0 | 132.8 |
| $0.5Na_4P_2O_7/Gd_2O_3$ at 1101 K | 531.2 | 133.3 |
| CaO at 1101 K | 528.5 | |
| Phosphide | — | 128.3–129.0 (*12*) |
| Phosphorus | — | 129.8 (*12*) |
| $Na_2HPO_4$ | — | 133.0 (*12*) |
| $Na_3PO_4$ | 530.3 | 132.3 (*14*) |
| $NaPO_3$ | — | 134.0 (*12*) |

indicated that the oxygen on $Na_4P_2O_7/CaO$ was more electron deficient than that of pure CaO. The binding energies of phosphorus were also similar on all three catalysts and comparison with the standards (Table 3) indicated that it did not exist in either the phosphide or the phosphorus state.

For sodium, however, it is difficult to differentiate chemical states based on the binding energy (*12, 13*). Therefore, Auger parameters (*12*), which give a better distinction between chemical states for sodium, were calculated. The Auger parameter is defined as the difference in binding energy between the photoelectron and the X-ray-induced Auger peak of sodium. A plot of the Auger parameter plus photon energy versus binding energy of sodium is shown in Fig. 11. It is clear that the chemical state of sodium on $Na_4P_2O_7/CaO$ is similar to those on pure $Na_4P_2O_7$ and on $Na_4P_2O_7/Gd_2O_3$.

The C 1*s* peak of $0.1Na_4P_2O_7/CaO$ is shown in Fig. 12. After the oxygen exposure at 1101 K, a carbon peak corresponding to hydrocarbon was observed. When the sample was exposed to methane/oxygen (2 : 1) mixture at 1101 K; an additional carbon peak corresponding to carbide was observed. The peak corresponding to carbide could be easily removed by subsequent exposures to oxygen. Thus, this carbide may be a precursor for carbon oxide formation. A carbon peak corresponding to carbonate (288.7 eV) was not observed. The peak at 290.2 eV which was present both before and after $CH_4/O_2$ exposures could be either bicarbonate or part of the sodium Auger (KLL) series. X-ray diffraction analysis also indicated the absence of $Na_2CO_3$ phase on the sodium pyrophosphate-containing catalysts before and after reactions.

*Surface acidity and surface area.* Results of the surface acidity tests are listed in Table 4. The data indicated that all catalysts except $Gd_2O_3$ had an acidity greater than 7.0 (the $pK_a$ value of *o*-nitrophenol) while $Gd_2O_3$ had an acidity close to 7.0. [The definition of acidity (*11*) used in this discussion is as follows: The acidity of the surface is comparable to the acidity of an aqueous solution which has a pH value close to the $pK_a$ value of an indicator which is present in both acid and base forms in that solution. Thus, the acidity of the surface was discussed in terms of the $pK_a$ of the indicator.] The BET nitrogen surface areas of $0.1Na_4P_2O_7/CaO$ and $0.1Na_2CO_3/CaO$ before the reaction were 6.2 and 5.5 $m^2/g$, respectively. The surface areas measured by krypton adsorption of both these catalysts after 24 h of reaction were 0.7 and 0.5 $m^2/g$, respectively.

## DISCUSSION

### *Relationship between Catalytic Performance and Elemental Composition of the Surface*

It was seen that both the $Na_2CO_3$ and $Na_4P_2O_7$ on CaO increased the $C_2$ yield considerably compared to pure CaO. Under similar experimental conditions, both $0.1Na_2CO_3/CaO$ and $0.1Na_4P_2O_7/CaO$ showed similar initial $C_2$ yield, but the deactivation on $0.1Na_2CO_3/CaO$ was drastic during 20 h (even below the $C_2$ yield of pure CaO), while $0.1Na_4P_2O_7/CaO$ produced a stable $C_2$ yield during 26 h (Fig. 1). It seemed that a very small amount of sodium

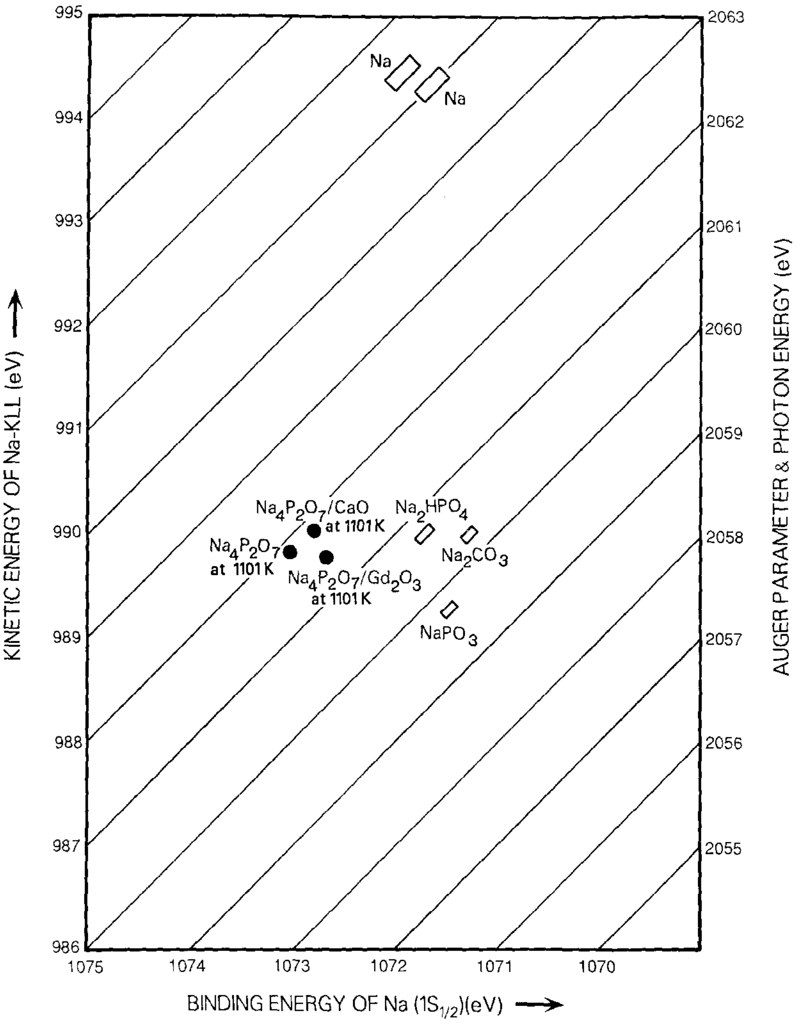

FIG. 11. Auger parameters of sodium on 0.1$Na_4P_2O_7/CaO$, 0.5$Na_4P_2O_7/Gd_2O_3$, $Na_4P_2O_7$, and standards.

TABLE 4

Results of Surface Acidity Tests on the Catalyst

| Indicator | Color in the acid form | Color in the base form | pH at color transition | Catalyst | Color on the catalyst | $C_2$ selecitivity (Me : $O_2$ = 5 : 1) |
|---|---|---|---|---|---|---|
| 1. Alizarin | Yellow | Red | 5.5–6.8 | CaO | Red | 40 |
| | | | | $Gd_2O_3$ | Red | 47 |
| | | | | $Na_4P_2O_7/CaO$ | Red | 60 |
| | | | | $Na_4P_2O_7/CaO$ | Red | 64 |
| 2. *o*-Nitrophenol | Colorless | Yellow | 5.0–7.0 | CaO | Dark yellow | |
| | | | | $Gd_2O_3$ | Light yellow | |
| | | | | $Na_4P_2O_7/CaO$ | Dark yellow | |
| | | | | $Na_4P_2O_7/Gd_2O_3$ | Dark yellow | |

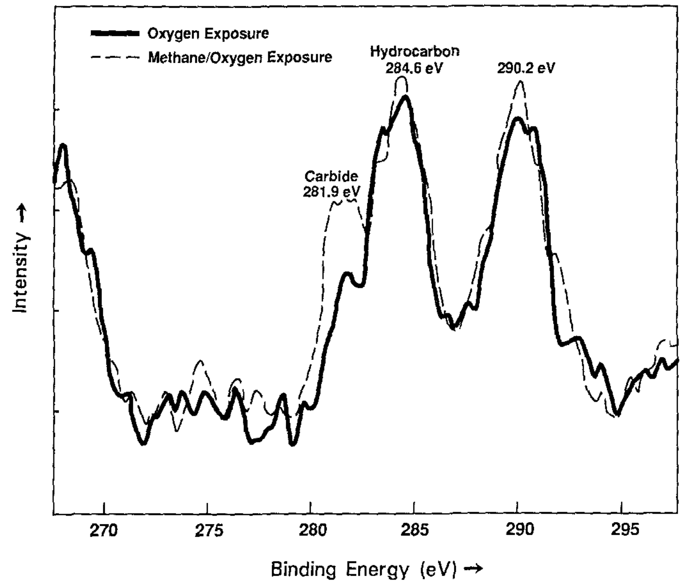

FIG. 12. XPS spectra of C 1*s* peak on $Na_4P_2O_7/CaO$.

on oxides produced lower $C_2$ yields when compared to that of pure oxides [$Gd_2O_3$ (Fig. 4) and CaO (*9*)]. This could be the reason for the low $C_2$ yield on $Na_2CO_3/CaO$ after 20 h. On $0.1Na_2CO_3/CaO$, there was a considerable loss in the amount of sodium on the surface (certain areas had zero sodium content) after the reaction, while on $Na_4P_2O_7/CaO$, a reasonable amount of sodium was retained on the surface even after 26 h of reaction. Comparison of Na/Ca ratios obtained by AAS and AES data indicated (Table 1) that the sodium was distributed mainly on the surface of the catalyst containing $Na_4P_2O_7$. After the reaction, there was no significant change in the total sodium in $Na_2CO_3$-containing catalysts even though the surface concentration was drastically changed. Thus, phosphorus seemed to have an ability to retain more sodium near the surface of the catalyst. However, in the catalyst containing $Na_2CO_3$ the loss of sodium from the surface could be due to evaporation and migration of surface sodium to the bulk. The initial Na/Ca ratio on $Na_4P_2O_7/CaO$ was about 0.26; it decreased to 0.14 during the first 3 h of reaction and remained essentially constant for the next 26 h. The $C_2$ yield also decreased from 19 to 18% during the first 3 h and remained constant for the next 26 h. The ratio of Na/Ca present on the $Na_2CO_3$/CaO surface before the reaction was about 0.10 which was similar to the Na/Ca ratio on $Na_4P_2O_7/CaO$ during 3 to 26 h of reaction. The presence of phosphorus on $0.1Na_4P_2O_7/CaO$ may have not contributed to an additional $C_2$ yield over the catalyst since both $Na_2CO_3/CaO$ and $Na_4P_2O_7/CaO$ resulted in similar $C_2$ yields initially. However, the presence of phosphorus had a significant contribution to the stability of the catalyst. The major contribution of phosphorus appears to be its ability to retain sodium on the surface for a longer period. It was also interesting to note that both Na/Ca and P/Ca ratios were not changed on the surface when $0.1Na_4P_2O_7/CaO$ was heated at 1101 K in an oven for 26 h without reactants. Thus, the initial loss of Na on $0.1Na_4P_2O_7/CaO$ occurred only in the presence of reactants. However, the P/Ca ratio did not change at 1101 K either in the presence or in the absence of the reactants.

Thus, phosphorus on the surface was not consumed during the reaction.

Comparing both $C_2$ yield data (Fig. 2) and AES data (Table 2), it is again possible to relate the catalytic activity to the amount of sodium present on $Gd_2O_3$. Both $0.1Na_2CO_3/Gd_2O_3$ and $0.5Na_4P_2O_7/Gd_2O_3$ produced a similar initial $C_2$ yield. The AES analysis showed that both surfaces of $0.5Na_4P_2O_7/Gd_2O_3$ and $0.1Na_2CO_3/Gd_2O_3$ initially had similar Na/Gd ratios. However, the loss of surface sodium after the reaction was drastic on $Na_2CO_3/Gd_2O_3$ compared to that on $Na_4P_2O_7/Gd_2O_3$ which correlated well with the decrease in $C_2$ yield. These results were consistent with what was observed on the CaO system. Thus, the function of phosphorus may be the stabilization of sodium on the oxide surface. The reason for the initial deactivation of $Gd_2O_3$ containing $Na_4P_2O_7$ between 0.05 and 0.1 (mole ratio) was not clear.

### *Effect of Basicity, Surface Area, and Active Centers on the Catalytic Performance*

Previous workers (*4*) have postulated that it was the basicity of the surface which was responsible for the production of $C_2$ compounds. There could be a considerable contribution from surface basicity since electron transfer is involved in the reaction. However, it is not clear whether it is possible to relate the production of $C_2$ compounds completely to the surface basicity. For instance, at room temperature (298 K), pure CaO was more basic than pure $Gd_2O_3$ as shown in Table 4 but the $C_2$ selectivity over pure $Gd_2O_3$ produced slightly higher $C_2$ yields at 1101 K compard to pure CaO. However, the surface acidity could change when the catalysts were heated to reaction temperatures (1101 K).

Centers of $[Na^+O^-]$ have been identified on the $Na_2CO_3/CaO$ system at 923 K by Lin *et al.* (*9*), and were postulated to be the active sites for the reaction. It was also stated by the same group of researchers (*2*) that sodium can be easily substituted on calcium because of the similarity in size of $Na^+$ (0.116 nm) (*10*) and $Ca^{2+}$ (0.106 nm) (*15*), and hence, $Na_2CO_3/CaO$ was a better catalyst than $Na_2CO_3/MgO$. At 1101 K, 0.5 $Na_4P_2O_7/Gd_2O_3$ produced $C_2$ yields similar to that of $0.1Na_4P_2O_7/CaO$, yet $Gd^{3+}$ (0.093 nm) (*15*) is smaller than $Na^+$ (0.116 nm). Thus, it is unlikely that there would be substitution of $Na^+$ for $Gd^{3+}$. Iwamatsu *et al.* (*10*) recently reported that $Na^+$–MgO produced high $C_2$ yields at 1073 K even though $Na^+$ is considerably larger than $Mg^{2+}$. Thus, either the centers produced on $0.1Na_4P_2O_7/CaO$ were different from $0.5Na_4P_2O_7/Gd_2O_3$ or both catalysts had similar centers which are not produced by substitution of metal ions with $Na^+$. It should also be noted that it was necessary to have 0.5 mol of $Na_4P_2O_7$ on $Gd_2O_3$ to produce a yield of $C_2$ hydrocarbons similar to that produced by 0.1 mol $Na_4P_2O_7$ on CaO. However, XPS analysis showed that oxygen, sodium, and phosphorus were in similar chemical states on $0.5Na_4P_2O_7/Gd_2O_3$ and $0.1Na_4P_2O_7/CaO$. Thus, it is reasonable to conclude that the active centers produced on $0.5Na_4P_2O_7/Gd_2O_3$ are similar to those on $0.1Na_4P_2O_7/CaO$ which cannot be formed by substitution of $Na^+$. Thus, the active centers at 1101 K on these phosphorus-containing catalysts must be different from those of $Na_2CO_3$-containing catalysts at 993 K.

The increase in $C_2$ yield resulting from addition of sodium could also be due partly to the decrease in surface area, as observed by other workers (*10*). However, Lin *et al.* (*9*) and Iwamatsu *et al.* (*10*) observed a continuous decrease in surface areas with increasing sodium coverage on Na/CaO. Yet, the $C_2$ yield on intermediate sodium coverage was higher than that on high sodium coverage.

Therefore, the increase in $C_2$ yield by addition of sodium pyrophosphate to CaO cannot be fully explained due to surface area effect, as also indicated by Jones *et al.* (*7*). Drastic decreases in surface areas were observed in both $0.1Na_2CO_3/CaO$ and

$0.1Na_4P_2O_7/CaO$ after 24 h of reaction yet the $C_2$ yields were significantly different after 24 h on the two catalysts. Thus, the differences in reactivity cannot be fully explained by the surface area effect. The morphological changes associated with the reaction on $Na_4P_2O_7/CaO$ indicated that there was surface restructuring during the reaction.

### *Reaction Mechanisms*

Several different reaction mechanisms (*1*, *5*, *9*) have been proposed by previous workers. Some mechanisms involve complete surface reactions (*1*), while other mechanisms (*9*) involve surface-initiated gas-phase reactions. Based on the data in the reactor study in the present investigation, some insight into the reaction mechanisms can be deduced.

There was no drastic decrease in $C_2$ product formation (Fig. 7) associated with the large increase in $CO_2$. Thus, this large increase in $CO_2$ formation with decreasing $CH_4$-to-$O_2$ ratio (from 2 to 1) cannot be easily accounted for by the oxidation of $C_2$ products formed during the reaction. Thus, there seems to be an independent route for the formation of $CO_2$ (majority) directly from $CH_4$, in addition to the oxidation-of-products route. This is consistent with the observations by previous workers (*2*, *5*, *9*).

It is more likely that carbon oxide formation could take place on the surface of the catalyst and carbide could be the precursor for this carbon oxide formation as observed by XPS measurements.

### *Effect of Temperature on the Catalytic Performance*

The $C_2$ yields over both $0.1Na_4P_2O_7/CaO$ and $0.5Na_4P_2O_7/Gd_2O_3$ increased with increasing temperature up to 1101 K (Figs. 5 and 6). The increase in $C_2$ selectivity and the changes in product distribution with temperature were similar for both catalysts. The effect of temperature on catalytic performance may be due to two reasons. One reason may be the increase in rates of reaction with increasing temperature. For instance, it has been found that the activation energies (*5*, *6*) for the formation of $C_2H_6$ and $C_2H_4$ were higher than that for the formation of $CO_2$. Thus, the increase in $C_2$ selectivity with increasing temperature can be attributed to the relative increase by reaction rates. Similar behavior with temperature has been observed by Otsuka *et al.* (*5*), Ito *et al.* (*2*), and Lin *et al.* (*9*).

In addition, it is important to consider the changes in the nature of the surface of the catalyst with temperature. Maximum performance occurs at different temperatures on different catalysts. For instance, $C_2$ selectivity continuously increased on $Sm_2O_3$ (*5*) when the reaction temperature was increased from 850 to 1023 K, and data beyond this temperature were not reported. However, on both $Li_2CO_3/MgO$ and $Na_2CO_3/CaO$ (*2*, *9*) systems, the optimum temperature was 993 K. The decrease in $C_2$ selectivity beyond 993 K was attributed to the further oxidation of $C_2H_4$ and $C_2H_6$. However, in the present study on both $0.1Na_4P_2O_7/CaO$ and $0.5Na_4P_2O_7/Gd_2O_3$, $C_2$ selectivities continued to increase with increasing temperature up to 1101 K. Furthermore, Otsuka *et al.* (*5*) reported higher activation energy for the formation of $C_2H_6$ than for the oxidation of $C_2H_6$ to $CO_2$. Thus, optimum temperature on different catalysts cannot be completely explained by further oxidation of the products. Production of the active centers due to the interaction between $Na_4P_2O_7$ and the catalyst must also be temperature dependent. If the sodium phase remains as $Na_4P_2O_7$, there would not be a high catalytic activity since pure $Na_4P_2O_7$ produced the low $C_2$ yields. In this work, it was observed that there was a considerable decrease in sodium on the surfaces of both $Na_2CO_3/CaO$ and $Na_2CO_3/Gd_2O_3$ at 1101 K, while sodium was retained on the surfaces of these two oxides containing $Na_4P_2O_7$ at 1101 K. Thus, the optimum temperature of the catalyst at which the highest $C_2$ yield was produced may also depend on the changes in the surface of the catalyst with temperature.

## CONCLUSIONS

Both $Na_4P_2O_7/CaO$ and $Na_4P_2O_7/Gd_2O_3$ were found to be active, selective, and stable catalysts for partial oxidation of methane. The $C_2$ yields obtained over these catalysts ranged from 17 to 19%. Catalytic performance resulted from a unique interaction between the sodium and the oxide surface. The active sites produced on surfaces of both $0.1Na_4P_2O_7/CaO$ and $0.5Na_4P_2O_7/Gd_2O_3$ increased $C_2$ product formation while decreasing $C_1$ product formation compared to pure oxides. Phosphorus on the surface of $Na_4P_2O_7/CaO$ was found to stabilize the sodium on the surface without being consumed during the reaction. The major $C_2$ product formed on the active catalyst was $C_2H_4$. The optimum $C_2$ yield was obtained at a methane-to-oxygen ratio of 2. Temperature affected catalytic performance significantly. This temperature dependence on $C_2$ selectivity and $C_2$ yield may be due to both the differences in activation energies of different reactions and the changes in the surface of the catalysts at different temperatures. Auger electron spectroscopic analysis data on elemental composition of the catalysts correlated well with catalytic performance data. The stability of the catalysts was found to be related to the ability to retain sodium on the surface as observed by AES. Changes in surface morphology during the reaction were found by scanning electron microscopy. This indicated there was restructuring of the surface during the reaction. XPS data indicated that chemical states of oxygen, sodium, and phosphorus on $0.1Na_4P_2O_7/CaO$ were similar to those on $0.5Na_4P_2O_7/Gd_2O_3$. Carbide formation was observed on the surface after methane exposures which could be the precursor for carbon oxide formation.

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