

Synthesis of Ethylene via Oxidative Coupling of Methane.

I. Determination of Active Catalysts

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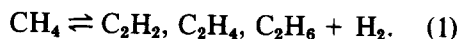
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Ethylene and ethane (C₂'s) have been synthesized by catalytic oxidative coupling of methane at atmospheric pressure and temperatures of 500–1000°C. A great number of metal oxides, supported on an α-alumina support, have been screened for activity and selectivity in the normal, concurrent feeding mode of reactants, as well as, in the sequential or feed programming mode. The concurrent feeding experiments gave low selectivities of 0–20%, while feed programming experiments gave selectivities of ~50%. In the latter case, however, a stainless-steel reactor became catalytically active for burning of methane to carbon oxides. Although a stainless-steel reactor was used in most of the work reported here, a quartz reactor was found to be inert. The most active catalysts for C₂ formation were the oxides of Sn, Pb, Sb, Bi, Tl, Cd, and Mn, while Li, Mg, Zn, Ti, Zr, Mo, Fe, Cr, W, Cu, Ag, Pt, Ce, V, B, and Al showed little or no activity. The low C₂-forming activity of Pt and Ce, however, may be due to the secondary burning of C₂'s on the stainless-steel reactor walls. This also makes it difficult to quantify the C₂-forming selectivity of the active metal oxides. The active metals seem to exhibit a common characteristic: they can cycle between at least two oxidation states. Although there are differences in selectivities in C₂ formation and carbon oxides formation, no correlation seems to exist with the free-energy changes in the oxidation states. A possible mechanism for C₂ formation from methane is proposed.

INTRODUCTION

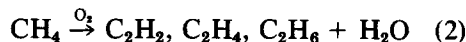
Shortages of prime feedstocks for ethylene manufacture have spawned numerous attempts to use different raw materials. Methane, one possible raw material, is by far the most abundant component of natural gas, usually comprising over 90 mole% of the hydrocarbon fraction of the gas. It therefore represents potentially a considerably more abundant precursor for ethylene than, e.g., ethane and propane, the two most widely used gaseous precursors. Methane's high molecular stability compared to other aliphatics, however, makes its use in ethylene production difficult, and no significant amount of ethylene is produced commercially from methane today.

One manifestation of this difficulty is shown in Fig. 1, where the equilibrium conversion to C₂ products via dehydrogenative coupling is shown as a function of temperature.



From this figure it is apparent that temperatures in excess of 800°C must be reached to effect practical conversions. Another problem is the high endothermic heat of reaction: 53 kcal/g mol ethylene versus 35 kcal/g mol for ethane dehydrogenation. This high endothermic heat is expensive to generate and transfer to the gas at high temperatures.

Oxidative coupling,



would appear to solve the thermodynamic-barrier and heat-of-reaction problems, but there is no indication that a highly selective reaction would result without the use of a catalyst. The primary objective of this study was to uncover selective catalysts for the oxidative coupling of methane to form C₂'s, and principally ethylene.

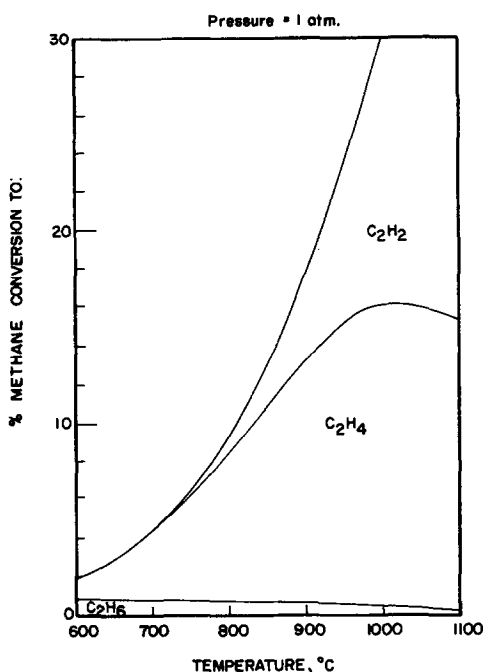


FIG. 1. Equilibrium conversions to C_2 products via dehydrogenative coupling.

A major problem in studying catalytic oxidative coupling is the presence of competing gas phase, noncatalyzed reactions. To eliminate or at least minimize noncatalyzed reactions, the reactor was operated cyclically, i.e., methane and air were fed one-at-a-time across the catalyst with short purging flows of nitrogen in between. A diagram of a typical feed program is shown in Fig. 2. Feeding in this fashion does impose another criterion on the catalyst: it must have the

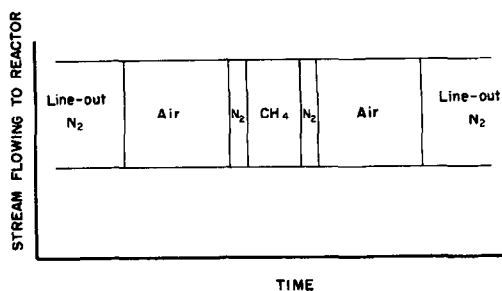


FIG. 2. Typical feed program.

ability to retain one reactant until the other reactant is fed.

Cyclic or periodic operation, varying feed composition, feed flow rate, and/or temperature, have been investigated experimentally and mathematically previously (1-7), but the objective of these studies was almost always that of increasing reaction rate or conversion. Seldom, if ever, can cyclic operation be justified on such a basis, however, since the complex controls and feeding systems required are more costly than installing a somewhat larger reactor which would give a comparable conversion.

Selectivity improvement via cyclic operation, on the other hand, is a different matter, and minimizing raw material costs through improved selectivity represents an economically more realistic objective for producing large-volume chemicals. Ethylene clearly falls into this category. Thus an ancillary objective of this study was to explore whether selectivity improvement

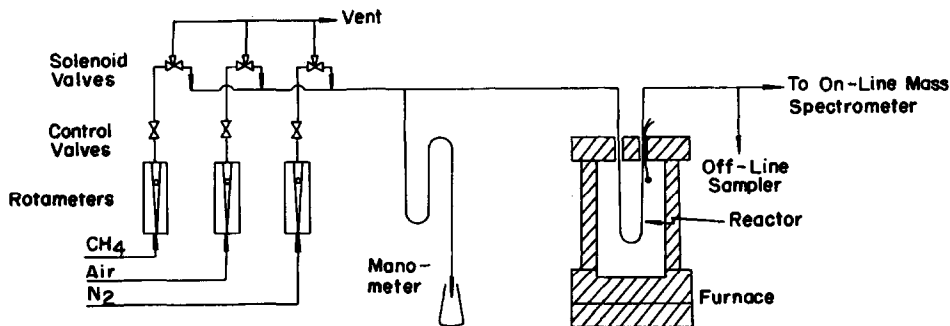


FIG. 3. Schematic diagram of catalyst testing reactor.

would result from cyclic operation.

This paper reports on early results of an extensive study of the cyclic oxidative coupling of methane to form ethylene.

EXPERIMENTAL

A. Reaction System

A diagram of the reaction system is given in Fig. 3. Most of the experimental work involved the use of a small fixed-bed reactor made of $\frac{1}{4}$ -in. (0.18-in. i.d.) stainless-steel tubing. The tubing was U-shaped and was placed in a radiant furnace. The normal catalyst charge was 2 ml (~ 2 g) of catalyst diluted with 8 ml of inert bare support. Catalyst and bare support were crushed and screened to give an 8×20 -mesh fraction.

Feeds to the reactor (air, nitrogen, and methane) were fed continuously through rotameters and needle valves for flow control. The gases then passed through three-way solenoid valves which were activated by timers. In general only one gas was fed to the reactor at a time. The timing device also controlled a servo motor which periodically advanced the setting on the furnace variac. This feature gave a more or less continuous temperature rise in the furnace. A typical "run" consisted of the following sequence of feeding steps (all flows = 0.2 g mol/hr):

Line-out flow of N_2 ,
60-sec pulse of air,
10-sec pulse of N_2 ,
30-sec pulse of CH_4 ,
10-sec pulse of N_2
60-sec pulse of air,
line-out flow of N_2 .

Equipment downstream of the reactor was minimal. The reactor effluent was piped directly to a General Electric mono-pole fast-scanning mass spectrometer inlet. There was also a provision for removing a gas sample for chromatographic analysis.

A few runs at the beginning of these tests were made in a tubular reactor consisting of a section of $\frac{1}{2}$ -in., schedule-40 stainless-

steel pipe (i.d. = 0.62 in.), which was wound with nichrome wire and insulated. Equipment on the upstream and downstream sides of the reactor was virtually identical.

B. Catalyst Preparation

All catalysts were prepared using standard impregnation techniques. In most preparations, nitrate salts were dissolved in distilled water and the resulting solution vacuum impregnated onto the α -alumina carrier (Norton Co. LA-956 and LA-4102, surface area of ~ 1 m²/g and density of ~ 1 g/ml). Typically, the impregnated carrier was dried in steps at 60°C/30 min and 110°C for 2–3 hr. Final heat treatment was at $\sim 700^\circ\text{C}$ for 1–3 hr. The amounts of active elements were typically between 5–10 wt%.

RESULTS

An early determination of the benefits of cyclic compared to steady flow operation was made using the $\frac{1}{2}$ -in. diameter reactor. A catalyst consisting of lead oxide supported on α -alumina was used. The charge consisted of 47 cm³ of this catalyst diluted with an equal volume of bare Filtros alumina. The results are shown in Table 1. In the first run, the feeds were added one-at-a-time across the catalyst, while in the second the feeds were added simultaneously. Flows were such that the same numbers of moles per hour of the three feeds were added in each experiment. Thus, both the gas-phase residence times of methane in the reactor and the average moles of methane fed per unit time per unit of catalyst were the same in both experiments. The partial pressure of methane in the cyclic experiment was higher—a situation which, if anything, one could speculate leading to a lower C_2 selectivity.

Analyses of the reactor effluents showed about a one-order-of-magnitude increase in the yield to C_2 's with cyclic operation compared to steady-flow operation. The major fraction of the C_2 's formed was ethylene,

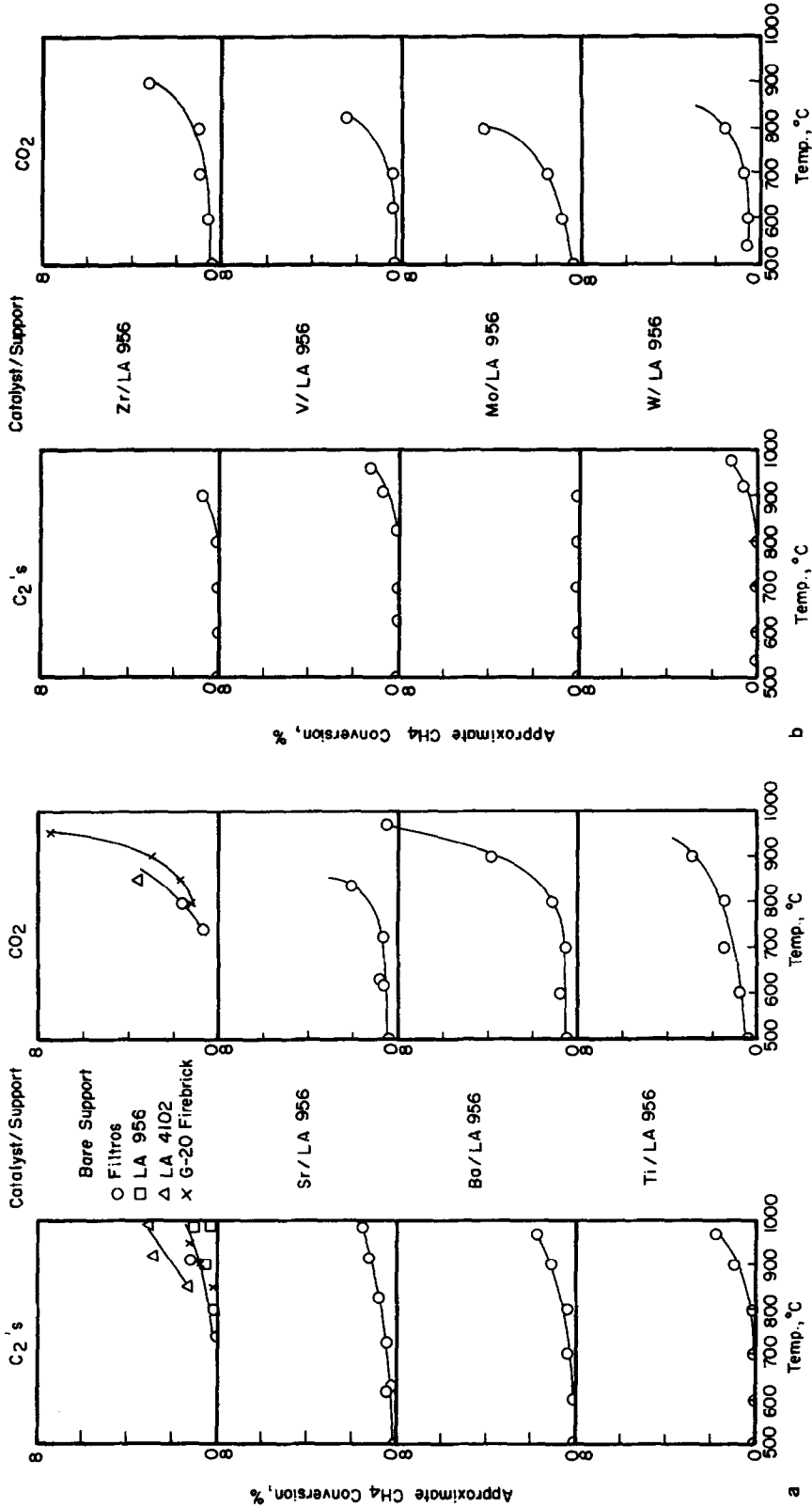


Fig. 4a-e. Approximate CH₄ conversion to C₂'s and CO₂.

ETHYLENE SYNTHESIS FROM METHANE

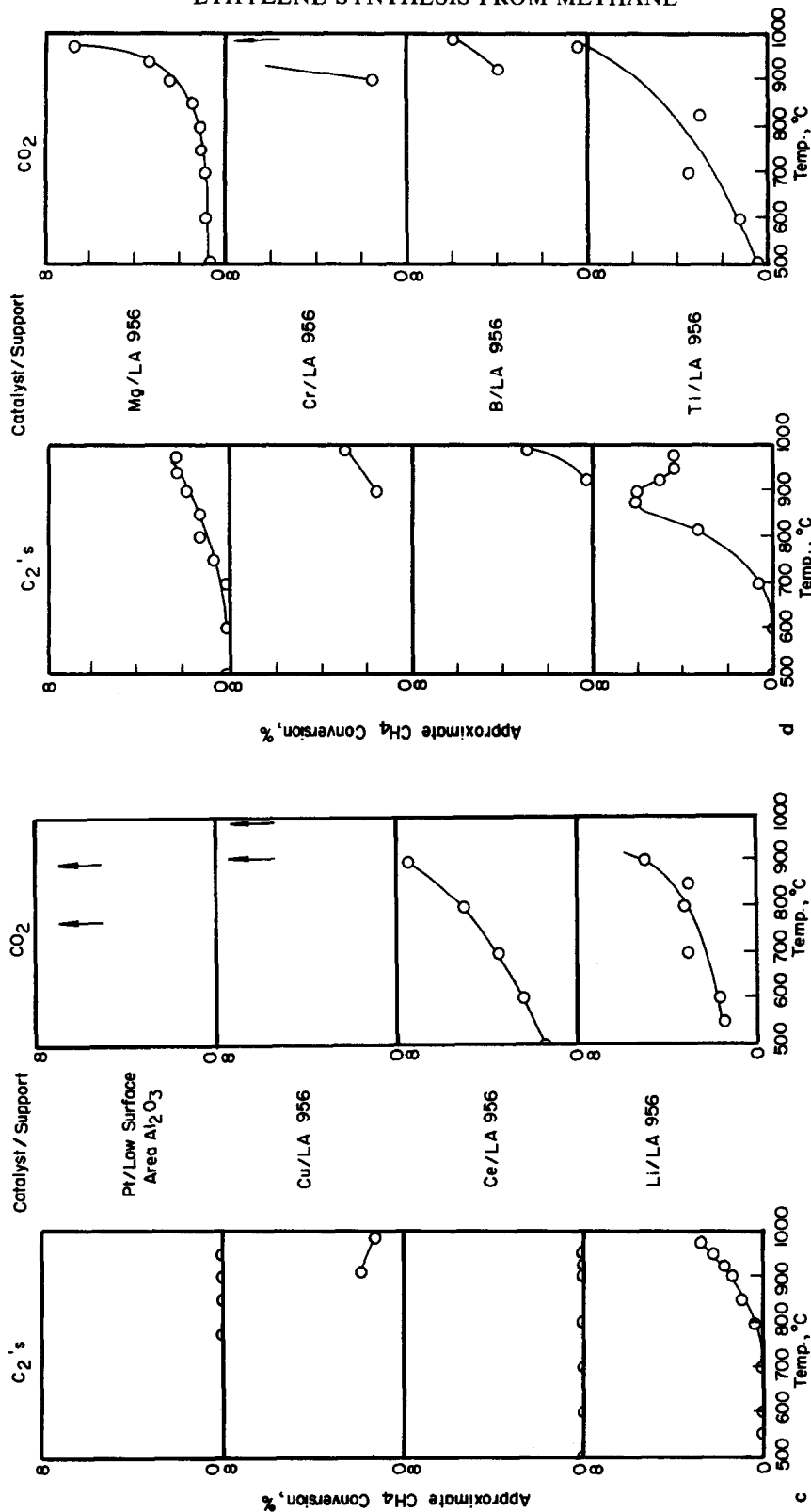


FIG. 4—Continued.

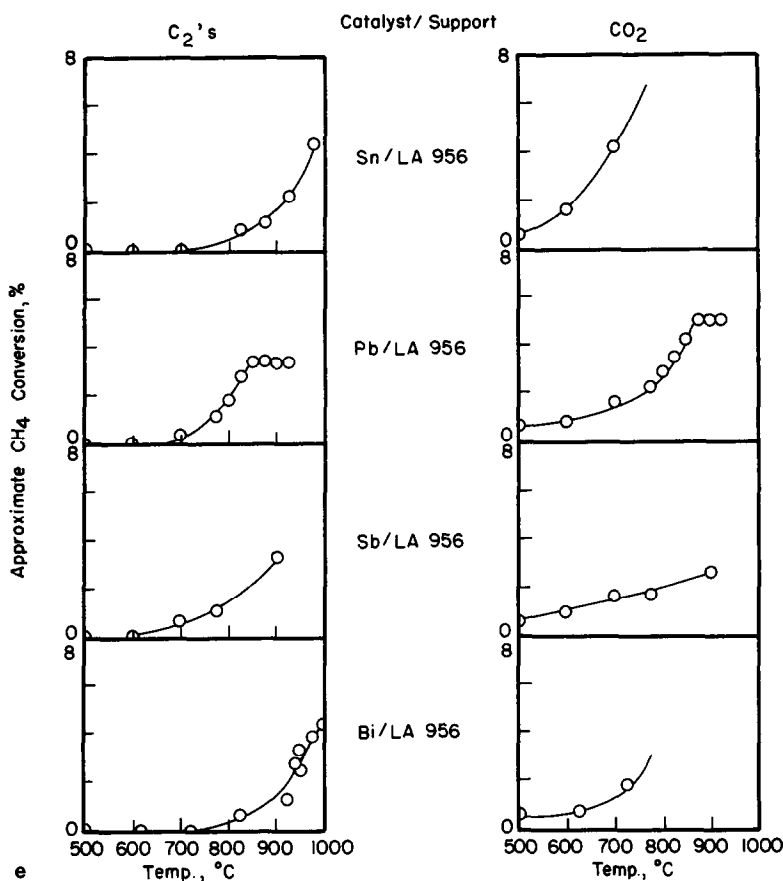


FIG. 4—Continued.

with small amounts of ethane and traces of acetylene also being formed.

A number of early tests were made, generally in the temperature range of about 600 to 1000°C, monitoring for the presence of C₂'s but not carbon oxides. Results of these tests are given in Table 2. From this table it can be seen that cobalt, manganese, cadmium oxides but probably not zinc oxide showed some C₂-forming activity. Iron, nickel, and silver were essentially inactive since activity at the 1–2% yield level is not higher than what would be expected in a noncatalyzed reaction. Later tests in this series were made monitoring both C₂'s and CO₂ (CO concentrations were essentially negligible) during the hydrocarbon-feed part of the cycle. Yields are shown in Figs. 4a–e. Several bare supports including

Filtros, Johns–Manville G-20 firebrick, and Norton LA956 and LA4102, were tested to give a noncatalyzed baseline. Those catalysts which promoted more C₂ formation than the baseline included oxides of tin, antimony, bismuth, lead, thallium, antimony, and perhaps lithium and boron.

All of these tests were made with the $\frac{1}{4}$ -in. reactor and with cyclic feeding. Flows of each stream were 0.2 g mole/hr, and the cyclic feeding schedule was that of Fig. 2.

The finding that bare supports seemed to promote the formation of CO₂ during the methane-feed part of the cycle in spite of the likelihood that they adsorbed little oxygen, raised the suspicion that the stainless-steel reactor wall might have been involved in CO₂ formation. Three cyclic-feeding tests were made using a $\frac{3}{8}$ -in. o.d. stainless-

TABLE 1

Comparison of C₂ Yields during Feed-Programming and Steady-Flow Modes of Operation^a

	Catalyst ^b : PbO on Norton LA 4102 alumina	
	Feed programming	Steady flow
	Feed Rates (g mol/hr)	
CH ₄	1.6	1.6
N ₂	0.8	0.8
Air	1.6	1.6
	Feed program (sec)	
CH ₄	20	None
N ₂ blanking pulse	5	
Air	20	
N ₂ blanking pulse	5	
Maximum C ₂ per pass yield	~10	~1

^a These tests were conducted in $\frac{1}{2}$ -in. schedule-40 pipe with a $\frac{1}{4}$ -in. axial thermowell. Reactor pressure was 6 psig and temperature ranged between 800 and 1000°C.

^b 47 ml of catalyst was diluted with 47 cm³ of bare support in these tests.

steel U-tube reactor and a similar diameter quartz U-tube reactor. Results are shown in Fig. 5, and they clearly support the contention that stainless-steel reactor wall was in fact the source of most of the CO₂ formation. For this reason no clear conclusions can be drawn from the data presented here regarding the selectivity to C₂'s.

TABLE 2

C₂-Forming Tendencies for Various Catalysts^a

Impregnating salt	Max. yield to C ₂ 's ^b (%)	Temp. at max. yield (°C)
Fe(NO ₃) ₂	1	N.M. ^c
Ni(NO ₃) ₂	1	N.M.
Co(NO ₃) ₂	3	1000
AgNO ₃	1	900
Zn(NO ₃) ₂	2	950
Mn(NO ₃) ₂	5	810
Cd(NO ₃) ₂	4	825

^a Support was Norton LA4102 alumina.

^b Includes small amount of C₂H₆.

^c N.M.-Not measured.

Reactor	Bare Support (20cc, 8x20 mesh)
○ 3/8" 304 SS	Carborundum Co. CLO9R SIC
□ 3/8" 304 SS	Johns-Manville Co. G-20 Firebrick
● 3/8" Quartz	Carborundum Co. CLO9R SIC

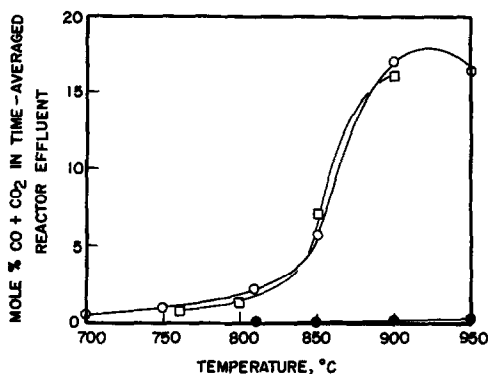


FIG. 5. Effect of reactor material of construction on losses to carbon oxides.

Periodically during these tests, an analysis was made for hydrogen. The amounts found were much less than would be expected for dehydrogenative coupling.

DISCUSSION

Nature of Catalysts

Figure 6 shows a periodic table listing the catalysts investigated and an indication as to whether or not they produced greater or lesser amounts of C₂'s than the bare supports. Inspection of this figure shows that the greatest region of activity corresponds to the so-called low-melting metals of IIIA, IVA, and VA and Mn of group VIIB and Cd from IIB. The surprising fact is that apparently some catalytic activity is possessed by quite a number of materials.

A further unusual fact is that the amount of oxygen transferred to the catalyst and subsequently to the coupling reaction during cyclic feeding is substantially larger than can be accounted for by simple monolayer coverage of the catalyst by oxygen. A monolayer coverage can be calculated from the following data and assumptions:

Catalyst support-2 g, with a surface area of 1 m²/g;

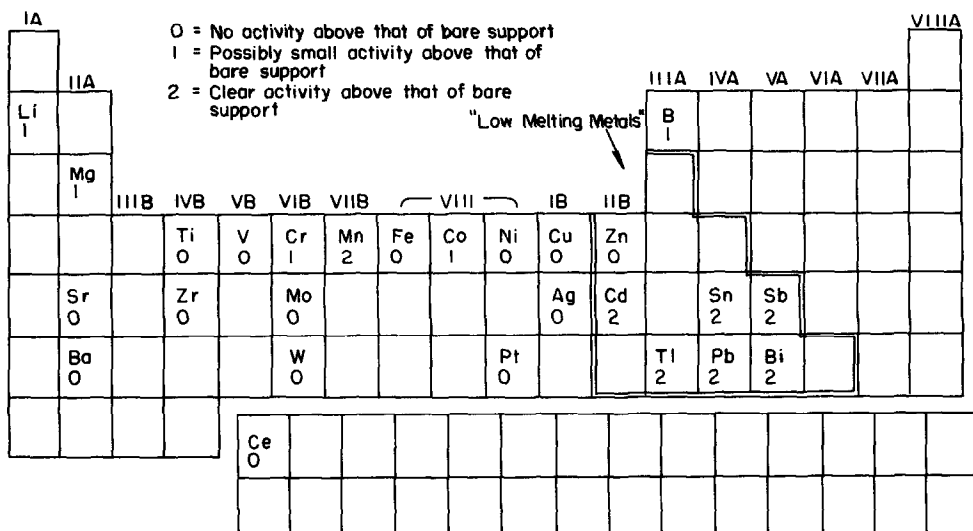


Fig. 6. Active and inactive catalysts for C_2 formation.

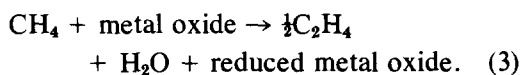
Catalyst completely covers the support surface or has an area roughly equivalent to that of the support;

Diameter of $O^{2-} = 2.8 \text{ \AA}$ (8), giving a cross-sectional area of about 6 \AA^2

The calculated monolayer coverage would be about $2.8 \times 10^{-5} \text{ g mol}$ of (equivalent) O_2 . On the other hand, if 5% of the methane fed during a cycle reacted via oxidative coupling to form ethylene at 50% selectivity, the oxygen required would be $1.3 \times 10^{-4} \text{ g mol}$ of O_2 . Thus the amount of oxygen required for such a coupling reaction is about an order of magnitude greater than the monolayer coverage. In fact, the catalyst very likely did not completely cover the surface of the support, and with some of the better catalysts the methane conversion was greater than 5%. It must therefore be concluded that the amount of oxygen stored and transferred by the active catalysts during cyclic operation was at least one order of magnitude larger than the amount which could be accounted for by monolayer adsorption on the catalyst surface.

The explanation for this situation seems to lie in hypothesizing that oxygen can dif-

fuse in and out of the bulk (subsurface atomic layers) of the catalyst, presumably oxidizing the metal to a higher valence state, during the air-flow part of the cycle. Then during the methane-flow part of the cycle, the oxygen can diffuse out to the catalyst surface and react with the methane. The stoichiometry of this latter step would thus be



One test of this hypothesis can be supplied by determining if reactions of the nature of Eq. (3) are thermodynamically allowable for the active catalysts. Free energies for these reactions were calculated from literature data (9) and are listed in Fig. 7. The activities of both the oxidized and reduced metals were assumed to be one, in lieu of detailed phase information. Figure 7 indicates that most of the catalysts showing oxidative coupling activity have one or more negative (favorable) or near-zero free energy changes for Eq. (3). Thus it appears possible that the cycling of the oxidation states of metals was occurring during the cyclic reaction. A possible mechanism for

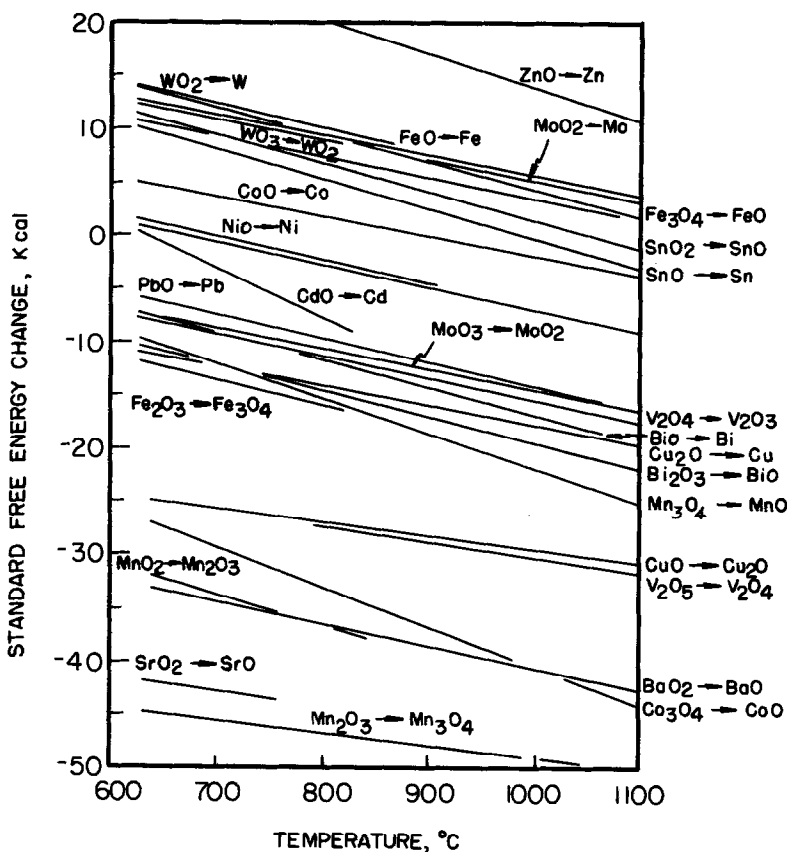
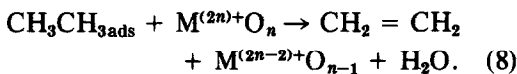
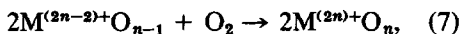
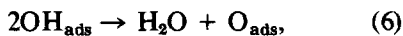
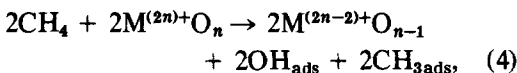


FIG. 7. Standard free energy changes for the reaction $\text{CH}_4 + \text{metal oxide} \rightarrow \frac{1}{2} \text{C}_2\text{H}_4 + \text{H}_2 + \text{reduced metal oxide}$.

the formation of C_2 's may involve these steps:



Where metal oxide, $\text{M}^{(2n)+}$ reduces to $\text{M}^{(2n-2)+}$ and oxidizes to $\text{M}^{(2n)+}$ to a depth of 10–12 layers.

Catalyst Selectivity and Activity

Inspection of the C_2 and carbon dioxide yields of the various catalysts shows

TABLE 3

More Active Elements for C_2 Formation

No.	Element	Methane conversion ^a to		
		C_2 's	CO_2	Total
	Blank (Support)	0.2	1.6	1.8
1	Mn	5	6.0 ^b	11 ^b
2	Cd	4.0	6.0 ^b	10 ^b
3	Sn	0.4	~8.0	8.4
4	Tl	3.0	3.8	6.8
5	Pt	<0.1	8.0	8.0
6	Ce	<0.1	5.0	5.0
7	Pb	2.0	2.6	4.6
8	Bi	0.4	4.0	4.4

^a At 800°C.

^b Estimated.

TABLE 4
Less Active Elements for C₂ Formation

No.	Element	Methane conversion ^a to		
		C ₂ 's	CO ₂	Total
	Blank (Support)	0.2	1.6	1.8
1	Mo	<0.1	4.0	4.0
2	Cu	n.m.	~4.0	4.0
3	Sb	1.5	2.0	3.5
4	Li	0.2	3.0	3.2
6	Mg	0.8	1.2	2.0

^a At 800°C.

definite differences in the ratios of these two species. Unfortunately, the finding subsequent to these tests that the source of much of the carbon oxides was associated with the metal reactor wall makes it impossible to determine inherent catalyst selectivities. Subtraction of the amount of carbon oxides formed with just bare support in the reactor is not warranted, since the rate of oxidation of C₂'s compared to methane is not known. Based on total conversion of CH₄ (to C₂'s and CO₂), approximate rankings of the more active elements and the less active elements are tabulated in Tables 3 and 4, respectively. Certainly, manganese, lead, thallium, cadmium, and antimony appear to exhibit high selectivity.

Process Considerations

It is clear that the catalysts tested here do not produce methane conversions high enough to be of commercial interest. A conversion of perhaps 25% or more to C₂'s would be required. Furthermore several of the metals or metal oxides have appreciable vapor pressures above 800°C. Nevertheless, the abundance of materials which exhibited oxidative coupling activity suggests that further research is warranted. Also, the cyclic feeding technique, besides producing a substantial efficiency increase to coupled products, provides a second important economic advantage. By properly diverting the reactor effluent stream the air used to oxidize the catalyst can be vented,

while the hydrocarbon effluent can be sent to a recovery unit. Such diversion eliminates most of the nitrogen from the recovery unit, thereby greatly reducing the recovery cost of ethylene.

CONCLUSIONS

The cyclic feeding of air and methane produced C₂'s (primarily ethylene) in the presence of a number of metal oxides. Most of these metals lie in the low-melting metal part of the periodic table, i.e., groups IIIA, IVA, and VA. The amount of oxygen transferred to the catalysts and then to the methane was many times larger than that which could have been adsorbed on the catalyst surface, indicating that oxygen must have diffused into and out of the bulk of the catalyst or at least, 10–20 atomic layer below the surface. Supporting this contention is the fact that all of the most highly active catalysts could store and release oxygen by cycling between at least two valence states.

Under cyclic feeding conditions, the stainless-steel reactor wall became active in catalyzing carbon oxides formation, the wall also apparently being able to store oxygen. Substitution of a quartz reactor for the stainless-steel reactor eliminated this problem.

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