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DIRECT CATALYTIC CONVERSION OF METHANE AND LIGHT HYDROCARBON GASES

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Prepared by: Robert B. Wilson Jr. and Yee Wai Chan

Prepared for:

U.S. DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236-0940

Attention: Mr. Lloyd Lorenzi, Project Manager

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Approved:

DDMacdonald
D. D. Macdonald, Laboratory Director
Chemistry Laboratory

MASTER

SRI International
333 Ravenswood Ave. • Menlo Park, CA 94025
(415) 326-6200 • TWX: 910-373-2046 • Telex: 334-486

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INTRODUCTION

The United States will need to be able to convert coal to liquid fuels should current supplies be interrupted. The indirect method for producing fuel liquids is the gasification of the coal to synthesis gas (syngas) followed by Fischer-Tropsch synthesis (FTS)[1] to convert syngas to hydrocarbons. However, both the gasifier[2] and the FTS[3,4] processes result in the production of methane and/or light hydrocarbon by-products that negatively affect the economics of the production of liquid fuel from coal. The goal of SRI's research is thus to develop catalysts that directly convert methane and light hydrocarbons to intermediates that can, as economics dictate, be subsequently converted either to liquid fuels or value-added chemicals.

In this program we are exploring two approaches to developing such catalysts. The first approach consists of developing advanced catalysts for reforming methane. We will prepare the catalysts by reacting organometallic complexes of transition metals (Fe, Ru, Rh, and Re) with zeolitic and rare-earth-exchanged zeolitic supports to produce surface-confined metal complexes in the zeolite pores. We will then decompose the organometallic complexes to obtain very stable, highly dispersed catalysts. The increased activity of highly dispersed catalysts is desirable for activating relatively inert methane, and highly dispersed catalysts are more resistant to coking. The use of zeolitic supports will stabilize the highly dispersed catalysts, and the acidic nature of the zeolite is likely to contribute to the reforming chemistry.

Our second approach entails synthesizing the porphyrin and phthalocyanine complexes of Cr, Mn, Ru, Fe, and/or Co within the pores of zeolitic supports for use as selective oxidation catalysts for methane and light hydrocarbons. Porphyrin and phthalocyanines are potent oxidants that also allow careful control of the active form of oxygen, thereby leading to control of activity and selectivity. The use of zeolitic supports will enhance the stability and reactivity of the catalysts and will discourage the secondary reactions that always pose problems in the oxidation of methane because the primary products are more easily oxidized than methane.

During the second quarter of this project, we concentrated on methane reforming. Two ruthenium clusters (Ru_4 and Ru_6) supported on three types of support materails (β-alumina, 5 Å molecular sieves, and γ-zeolite) were tested for methane reforming. The effects of cluster size, supporting material, and reaction conditions were evaluated. The methane conversions range from 1.74 to 10.11% at 750°C. The reaction product contains hydrogen, C_2 hydrocarbons, and C_6 or higher hydrocarbons. Up to 48.34% yield of hydrocarbon (C_2+) is obtained based on reacted methane. Some of these catalysts show very good coking resistance compared with a commercial ruthenium catalyst. Addition of oxygen to these reactions significantly increases the percent methane conversion at lower reaction temperature. However, carbon dioxide and water are the major products in the presence of oxygen.

TECHNICAL APPROACH

SRI's development of improved catalytic processes for the direct conversion of methane and light hydrocarbon gases to olefins or alcohols consists of four tasks. The tasks represent two approaches to the problem. In Tasks 1 and 2, we seek to develop advanced reforming catalysts for the use in production of olefins. These catalysts will consist of highly dispersed, very stable metal particles that are produced by the decomposition of surface-confined metal clusters of controlled size and configuration. In Tasks 3 and 4 we seek to develop oxidation catalysts of high activity that selectively produce alcohols. We will prepare catalysts by synthesizing known homogeneous oxidation catalysts in the pores of zeolite supports. The four tasks are described in more detail below.

Task 1: Synthesis of Advanced Reforming Catalysts for Methane

We will synthesize methane-reforming catalsts in Task 1 by thermally decomposing surface-confined metal clusters of carefully controlled size. The variables we will study include cluster size, cluster composition, and activation procedures. The support materials we will investigate are zeolites and rare-earth-exchanged zeolites; the metal complexes to be studied are the low-valent complexes of Re, Fe, Ru, Rh, and/or their mixtures. Clusters of 2-4 metal atoms will be used as catalyst precursors. The Re and Ru examples will be emphasized.

Research is under way* on the techniques of surface confinement to produce novel catalysts for a wide variety of processes.[5-25] The stability of surface-confined carbonyl clusters has been questioned.[26]

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*SRI's study of the techniques for HDN catalysis, DOE Contract No. DE-FG22-85P8C80906, and of FTS catalysis, DOE Contract No. DE-AG22-85PC80016.

Therefore, to prepare catalysts whose surface binding is better characterized, we will study catalysts of the Yermakov type, which are anchored by direct reaction with the surface [equation (1)].

$$RM_xL_n + HO\text{-(surface)} \longrightarrow RH + L_nM_x\text{-O-(surface)} \qquad (1)$$

Alkyl metal complexes are known for all the metals in question.[27]

Specifically, we are attempting to generate surface-confined metal complexes by using equation (1); we will start with the following compounds: For Re, we will use $Re_2(CH_2SiMe_3)$ or $Re_3(CH_3)_9(Py)_3$; for the Fe complexes, $Fe(allyl)_3$; for the Ru complex, $Ru_2(CH_2CMe_3)_6$; and for the Rh complexes, Rh_2(2-hydroxy-6-methylpyridine). Clusters will be prepared from the hydridocarbonyl clusters by relying on reactions such as (2) and (3).

$$H_2Ru_3(CO)_{11} + AlEt_3 \longrightarrow 2EtH + EtAlRu_3(CO)_{11} \qquad (2)$$

$$EtAlRu_3(CO)_{11} + HO\text{-(surface)} \longrightarrow EtH + (CO)_{11}Ru_3Al\text{-O-(surface)} \qquad (3)$$

The carbonyl clusters to be used include $H_2Ru_3(CO)_{11}$, $H_2Ru_4(CO)_{13}$, and $H_2Ru_6(CO)_{18}$ for Ru, and the mixed Fe/Ru clusters $H_2FeRu_2(CO)_{11}$, $H_2RuFe_2(CO)_{11}$, $H_4Ru_3Fe(CO)_{12}$, and $H_4Ru_2Fe_2(CO)_{12}$.

Characterizing the surface-confined complexes is the key to understanding their stability and activity.

Task 2: Testing of Methane Reforming Catalysts

SRI will test the methane-reforming catalysts in two phases. Phase 1 will consist of screening tests to determine relative catalytic activity and the effects of pretreatment. In Phase 2 we will incorporate a membrane in the reactor for hydrogen control.

Phase 1 will be conducted in a fixed-bed isothermal microreactor in a down flow mode at atmospheric pressure. An automated Carle two-column GC will be used to follow the conversion of methane and product formation. Variables will include space velocity and temperature. A commercially available platinum-based reforming catalyst (such as the Chevron catalyst) will be used as the baseline.

In Phase 2, we will design and build a reactor that will be equipped with an in-situ stabilized Pd membrane to control the H_2 partial pressure[28] (see Figure 1). Variables to be studied will also include space velocity of methane, temperature, hydrogen pressure, and hydrogen flow rate.

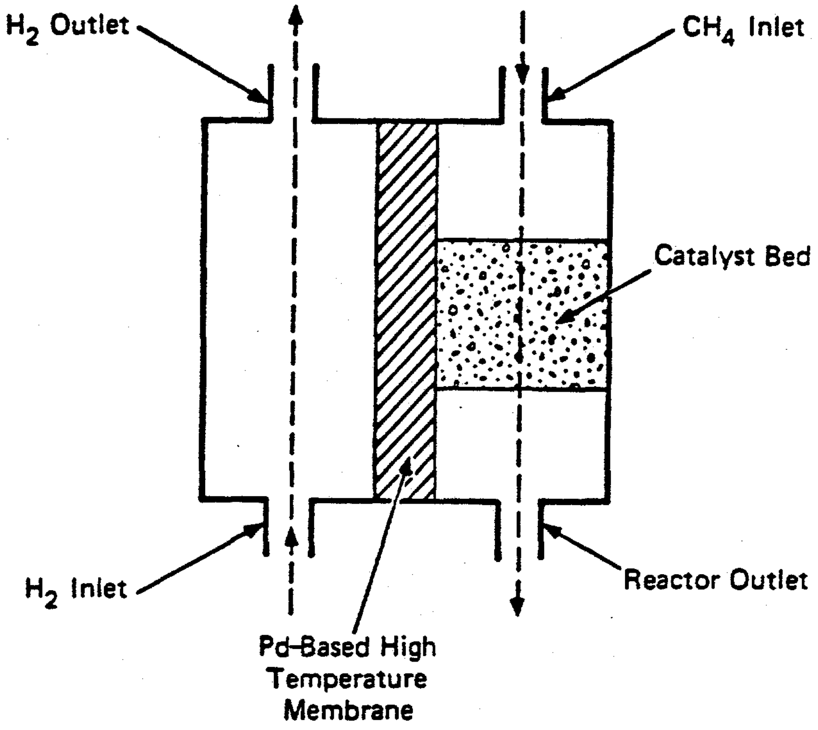

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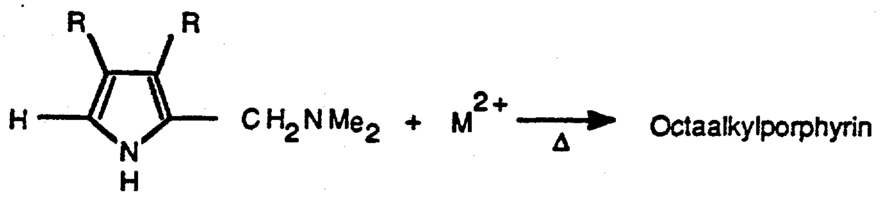
FIGURE 1 SCHEMATIC OF REACTOR WITH MEMBRANE FOR HYDROGEN CONTROL

Task 3: Synthesis of Oxidation Catalysts for Methane

In Task 3, SRI will synthesize oxidation catalysts by encapsulating porphyrin and phthalocyanine metal complexes in zeolites. Variables to be studied include the porphyrin or phthalocyanine ligand, the type of metal, and the type of zeolite. The metal complexes studied will be Cr, Mn, Re, Ru, and/or Co, with emphasis on the Ru examples.

The porphyrin and phthalocyanine complexes will be synthesized within the zeolite pore by first exchanging the metal ion into the pore, followed by template condensation.[29] For porphyrins the condensation of substituted pyrroles [equation (4)] will give the desired porphyrin.



(4)

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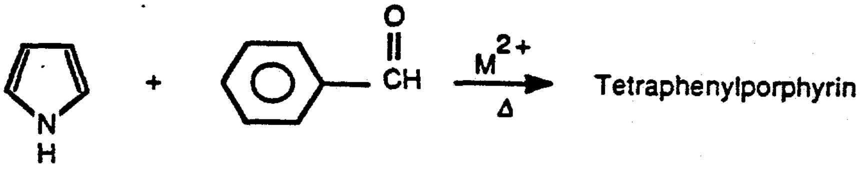
Alternatively, the cocondensation of pyrrole with benzaldehyde will give tetraphenylporphyrin [equation (5)].[30]



(5)

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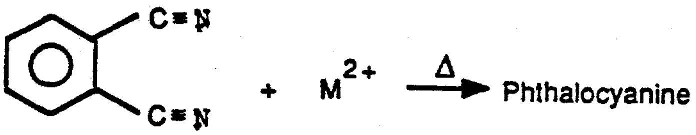
The phthalocyanines are produced by the condensation of phthalonitriles [equation (6)].



(6)

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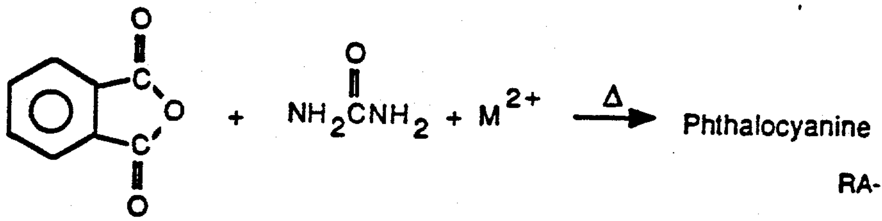
Alternatively, the condensation of phthalic anhydride and urea produces phthalocyanine [equation (7)].[31]



(7)

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Task 4: Testing of Methane Oxidation Catalysts

SRI will test methane oxidation catalysts in the same fixed-bed isothermal down flow reactor used in Task 2. We will use an automated two-column GC to follow the conversion of methane and oxygen and product formation. Low oxygen concentrations will be used initially. Variables will include space velocity, temperature, and feed composition. For comparative purposes, a commercially available oxidation catalyst will also be used, such as an bismuthmolybdate catalyst (Sohio) or vanadium pentoxide (American Cyanamid). Finally, mixtures of light hydrocarbons will be tested.

General Methods

The reactions will be conducted in the fixed-bed isothermal microreactor described above.[32-34] The exhaust gases from the reactor will be passed through a trap for liquid removal and then through a sampling valve for periodic sampling by the automated two-column Carle GC. The liquids will be analyzed by a second GC (HP5890) or a high pressure liquid chromatograph (HP1090).

A key concern is physically characterizing the catalysts.[35,36] The catalysts will thus be characterized before and after each run, without exposure to ambient conditions, by measuring the IR and UV-VIS spectra, oxidation state, and dispersion. Dispersion is a key point and will therefore be measured by three independent methods.

The chemical nature of the catalysts will be determined by spectroscopic techniques. Basset and Choplin have shown that UV-VIS can be used to characterize surface-confined catalysts.[16] The technique should be particularly good for the porphyrin and phthalocyanine catalysts because their characteristic UV-VIS bands are strong. IR will be measured and compared with literature studies of surface-confined clusters.[35-39] In addition, Ozin and coworkers have recently used far-IR bands to establish the presence of M-M bonds in zeolite-supported metal catalysts.[40-41]

SRI will use Auger and/or ESR spectroscopy to determine the oxidation state(s) of the confined metal catalysts spectroscopy.

We will use three independent methods to determine dispersion. First, the gross loading can be calculated from the results of elemental analysis. Dispersion can be determined by atomic absorption (AA), and BET will be used to measure surface area. Dispersion particle size will also be examined by high-resolution electron microscopy, which is accurate to a resolution of ~10 Å.[42-48] Finally, far-IR absorption can be used to calculate average particle sizes of about 20 Å and will be used to confirm other measurements.

RESULTS AND DISCUSSION

During the second quarter of this project, we concentrated on the testing of methane reforming catalysts (Task 2). A reactor system that included online GC analysis was built during this period. We tested seven ruthenium catalysts using this system. The results show that the supported Ru clusters are effective in reforming methane. At 750°C, up to ~ 50% of the reacted methane is converted to hydrocarbon products. We evaluated the effects of catalysts dispersion, cluster size, supporting material, and reaction conditions (temperature, pressure, space velocity) to the methane conversion and product distribution. We also investigated the oxidative coupling of methane by adding small amount of oxygen to the reactor. The results indicated that these ruthenium catalysts are active for methane oxidation as well as methane reforming.

Task 1. Synthesis of Advanced Reforming Catalysts for Methane

The ruthenium catalysts used in this research were synthesized in our laboratory on another research project,* and the synthesis and characterization of these catalysts are reported in detail in the Quarterly Technical Progress Report No. 4. We therefore only briefly describe our method of preparation.

The synthesis of these catalysts involves three steps. The first step is to synthesize the ruthenium cluster precursors. The second step is a novel approach developed in our laboratory that involves the reaction of the organometallic clusters with alkyl aluminum. The final step is to anchor these catalysts on supports by a chemical reaction

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*"Improved Fischer-Tropsch Synthesis for Indirect Coal liquefaction", DOE Contract No. De-AG22-85PC80016, SRI Project No. 1245.

between the hydroxyl groups of the support and the alkyl groups of the organometallic cluster to give a covalent chemical bond.

Two ruthenium clusters $H_4Ru_4(CO)_{12}$ and $H_2Ru_6(CO)_{18}$ were used as the precursors. The tetrahydridoruthenium carbonyl was prepared by a method developed in our laboratories, the direct reaction of triruthenium dodecacarbonyl with hydrogen in hexamethyldisilazane (HMDS) at elevated temperature.

$$4/3\ Ru_3(CO)_{12} + 2H_2 \xrightarrow[135^\circ C]{HMDS} H_4Ru_4(CO)_{12} + 4(CO) \qquad (7)$$

The hexaruthenium cluster was synthesized by Shore's method.[49] Triruthenium dodecacarbonyl is reduced by sodium benzophenone metal and then acidified.

$$Ru_3(CO)_{12} + Na[Ph_2(CO)] \xrightarrow[25^\circ C]{THF} 1/2\ Na_2[Ru_6(CO)_{18}] \qquad (8)$$

$$Na_2[Ru_6(CO)_{18}] + 2HCl \xrightarrow[25^\circ C]{THF} H_2Ru_6(CO)_{18} + 2NaCl \qquad (9)$$

Both the tetraruthenium and the hexaruthenium hydridocarbonyl complexes react readily with triethyl aluminum at room temperature.

$$H_4Ru_4(CO)_{12} + Et_3Al \xrightarrow[25^\circ C]{THF} (Et_2Al)Ru_4H_3(CO)_{12} + EtH \qquad (10)$$

$$H_2Ru_6(CO)_{12} + Et_3Al \xrightarrow[25^\circ C]{THF} (Et_2Al)Ru_6H(CO)_{18} + EtH \qquad (11)$$

The reaction stoichiometries were determined by measuring the quantity of ethane produced. These alkyl aluminum carbonyl ruthenium clusters are then used to react with the supports, as shown in reactions (12) and (13). Three types of supports, β-alumina, 5 Å molecular sieves, and LZ-γ5Z zeolite were used.

$$(Et_2A)Ru_4H_3(CO)_{12} + \text{support-OH} \xrightarrow[25^\circ C]{THF} \text{support-O-Al(Et)}Ru_4H_3(CO)_{12} + EtH \qquad (12)$$

$$(\mathrm{Et_2Al})\mathrm{Ru_6H(CO)_{18}} + \text{support-OH} \xrightarrow[25^{\circ}\mathrm{C}]{\mathrm{THF}} \text{support-O-Al(Et—}\mathrm{Ru_6H(CO)_{18}} + \mathrm{EtH} \quad (13)$$

Task 2: Testing of Methane Reforming Catalysts

The six ruthenium catalysts synthesized in Task 1 were tested for activity toward methane reforming. Tests were conducted in an isothermal down-flow microreactor. Products of the reforming reaction were determined by GC. The variables studied include temperature, pressure, space velocity, and catalyst. The effect of reaction temperature is similar for every catalyst. Figure 2 shows the correlation of reaction temperature and methane conversion. Higher methane conversion and product yield are obtained at higher temperature. These results are expected because reforming of methane is a thermodynamically unfavored process.[50] Increasing the reaction pressure has a similar effect on the methane conversion, as shown in Figure 3. However, the product selectivities for hydrogen and C_2 hydrocarbons decrease. The selectivities to C_6 or higher hydrocarbons increases with the reaction pressure (Table 1). Highest selectivity is obtained at 150 psig. Because our calculations are based on hydrocarbons of six carbon numbers, significant yield of higher carbon number hydrocarbons will decrease the numeric value. In other words, at higher pressure, the reaction could be producing more high molecular weight hydrocarbon (e.g., C_{10} or higher) than low molecular weight hydrocarbon (e.g., C_6 or C_7). These C_6+ products need to be separated further to gain a better understanding of the pressure effect. Increasing the space velocity (flow rate) has the opposite effect. The methane conversion significantly decreases but the selectivities to hydrocarbon products increase.

Coking is a general problem of heterogeneous catalyst and causes deactivation of the catalyst. The catalytic activities of these ruthenium catalysts as reflected by the methane conversion during a 12-hr reaction are shown in Figure 4. The zeolite and alumina-supported catalysts behave similarly in that the methane conversion decreases

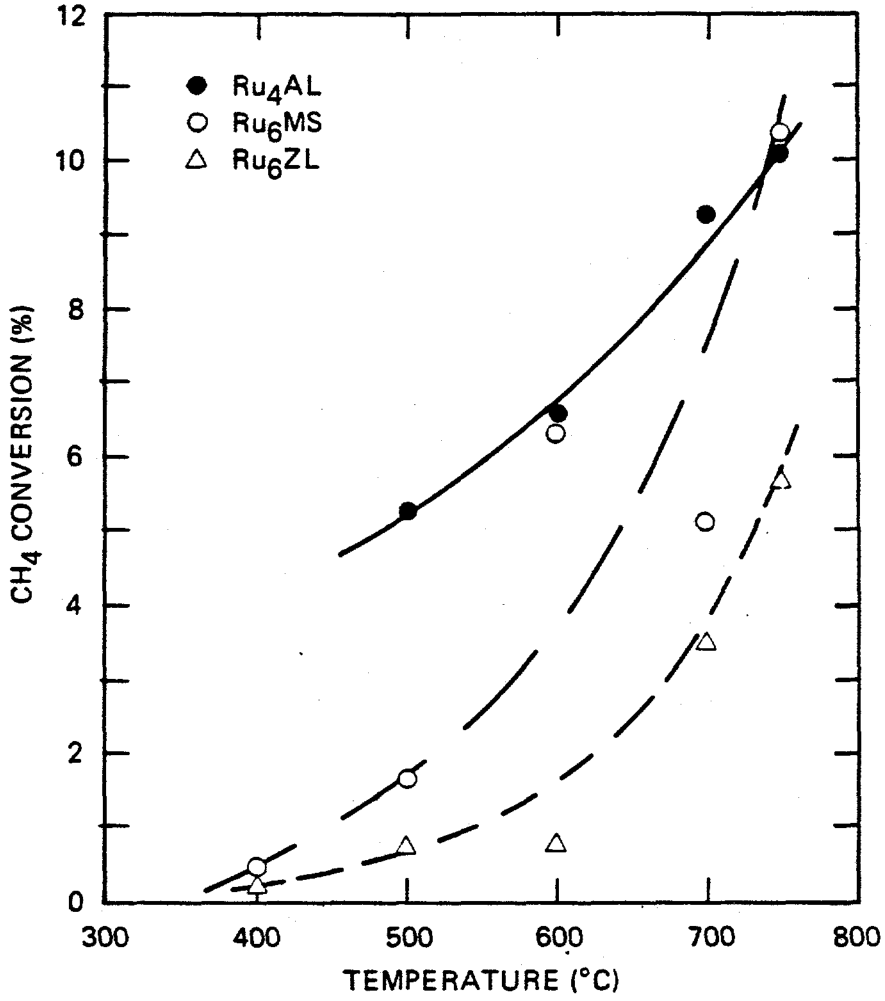

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FIGURE 2 CORRELATION OF REACTION TEMPERATURE AND THE PERCENT METHANE CONVERSION
Reaction Conditions: pressure = 50 psig, flow rate = 50 mL/min

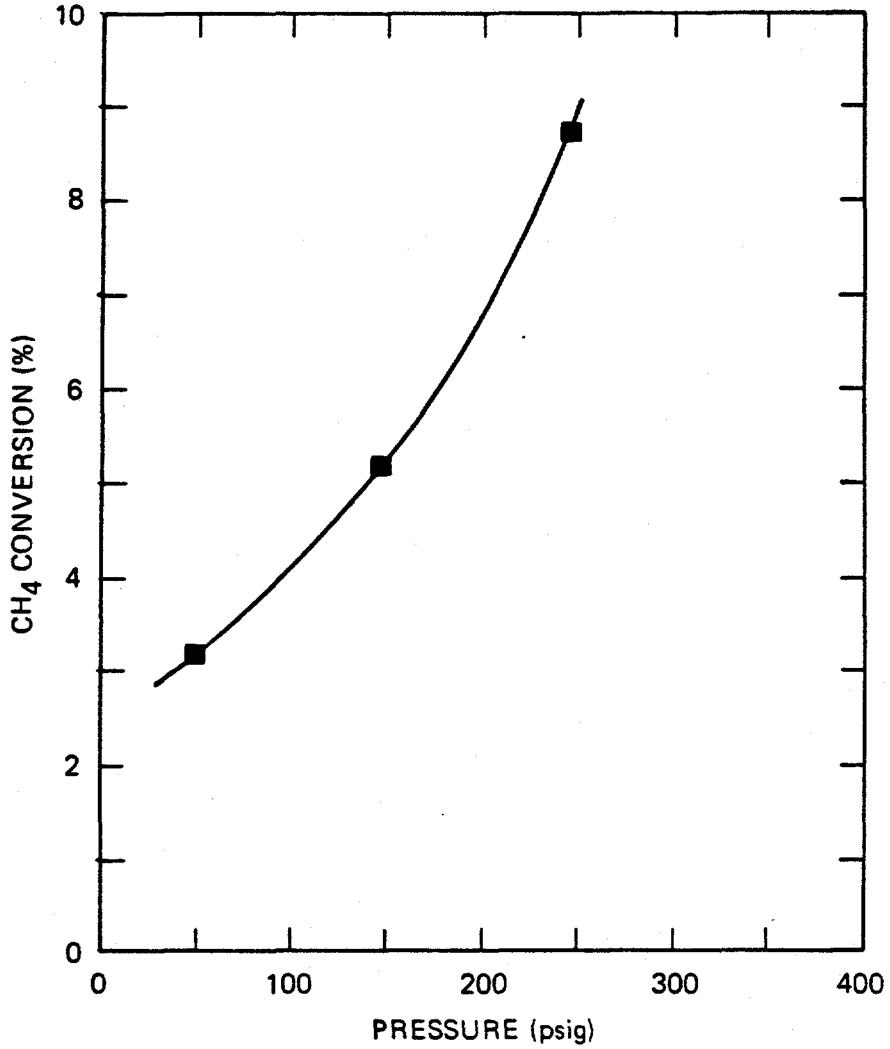

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FIGURE 3 CORRELATION OF REACTION PRESSURE AND THE PERCENT METHANE CONVERSION ON Ru_6ZL CATALYZED METHANE REFORMING
Reaction Conditions: temperature = 750°C, flow rate = 50 mL/min

Table 1

EFFECT OF REACTION PRESSURE TO THE METHANE CONVERSION AND PRODUCT DISTRIBUTION ON Ru_6ZL CATALYST AT 750°C

Pressure (Psig)	Flow Rate (mL/min)	$\%CH_4$ Conversion	% Selectivity of[b] H_2	C_2	C_6+
50	50	3.18	164.16	6.04	6.60
150	50	5.19	91.33	4.48	10.70
250	50	8.64	82.41	2.46	7.38
250	100	2.62	177.10	9.24	20.64

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[a] Ru_6ZL = zeolite supported $(C_2H_5)_2AlRu_6H(CO)_{18}$.

[b] Selectivities to hydrocarbons are based on carbon number and the amount of methane reacted.

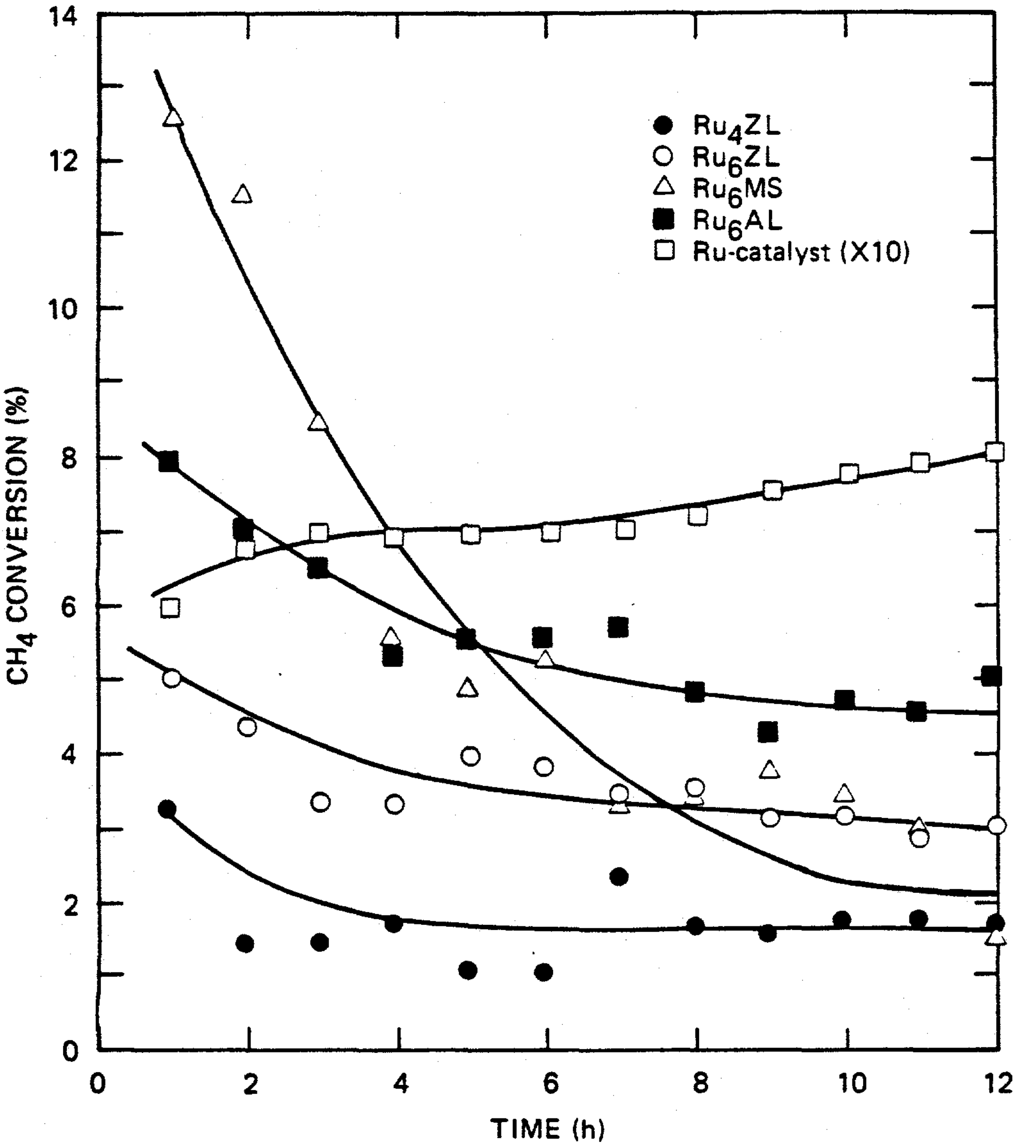

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FIGURE 4 PERCENT METHANE CONVERSION AS A FUNCTION OF TIME DURING A 12 h REACTION
Reaction Conditions: pressure = 50 psig, temperature = 750°C, flow rate = 50 mL/min.

Table 2

CATALYTIC REACTION OF METHANE REFORMING

Catalyst[a]	Ru (wt%)	Temp. (°C)	Flow Rate (mL/min)	CH_4[b] Conversion (%)	Selectivity to[b,c] H_2(%)	C_2(%)	C_6+(%)
Ru-Cat	0.5	750	50	71.24	151.04	--[d]	--
Ru_4AL	0.61	750	100	10.11	78.60	1.62	--
Ru_4MS	0.49	750	100	4.90	146.60	3.52	--
Ru_4ZL	0.61	750	50	1.74	25.28	6.90	28.92
Ru_6AL	1.26	750	50	6.06	113.39	6.94	41.40
Ru_6MS	0.19	750	50	5.56	192.80	1.00	14.76
Ru_6ZL	0.20	750	50	3.60	161.94	3.62	9.96

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[a] Abbreviation of $Ru_4 = (C_2H_5)_2AlRu_4(CO)_{12}$; $Ru_6 = (C_2H_5)_2AlRu_6H(CO)_{18}$. AL = βaluminum, 5-Å molecular sieve, ZL = LZ-γ52 zeolite. Ru-Cat is a commercial ruthenium catalyst obtained from Engelhard.

[b] Except for Ru_4AL and Ru_4MS, data are averaged from a 12-hr run and recorded in 1 hour intervals. For Ru_4Al and Ru_4MS, data are averaged from a 2-hr run and recorded in 1/2-h intervals.

[c] Selectivities to hydrocarbons are based on carbon number and the amount of methane reacted.

[d] Not detected.

during the first 2 hours of reaction and then reaches steady state. The 5 Å molecular-sieve-supported Ru_6 catalyst has a very high methane conversion at the beginning of the reaction but its activity decreases gradually. The commercial ruthenium has a totally different activity. The methane conversion is about ten times higher than our Ru clusters and its activity slowly increases during the reaction.

Our intention in using different supports is to confine the ruthenium cluster at different location on or within the support. Hence, the Ru_4 and Ru_6 cluster are dispersed on the alumina surface but are confined inside the pores of zeolitic supports. The pore size of 5Å molecular sieves is too small for the Ru_6 cluster but should be large enough for the Ru_4 cluster after decomposition. We expect different reactivity for the clusters on different supports. Our results summarized in Table 2 show that the alumina-supported Ru_4 and Ru_6 clusters give higher methane conversion than the same cluster or the other two supports. The commercial ruthenium catalyst is a mono-ruthenium unit, which should have a higher dispersion. Indeed, it has a much higher methane conversion than the Ru clusters. The methane conversions of the zeolite-supported catalyst are lower than the other catalyst, suggesting that the Ru clusters are located inside the zeolite cage. The rate of the reaction is determined by the rate of methane entering the zeolite cage and/or the rate of product escaping from the zeolite cage.

The size of the cluster (Ru_4 vs Ru_6) also affects the methane conversion and the product yield. In the cases of molecular sieves and zeolite supports, the Ru_6 cluster has higher activity than the Ru_4 cluster. The results on alumina support are different probably because of the higher dispersion of the smaller cluster. Since our results on the Ru_4AL and Ru_4MS are averaged from 2-hr reactions and the others are averaged from 12 h reactions, these data may not be reliably compared. Further studies on the cluster size effect are planned.

We also tried the oxidative coupling reaction of methane reforming [equations (14) and (15)] because these reactions are thermodynamically favored.[50]

$$nCH_4 + \frac{n}{2} O_2 \longrightarrow C_nH_{2n} + nH_2O \qquad (14)$$

$$nCH_4 + \frac{n-1}{2} O_2 \longrightarrow C_nH_{2n+2} + (n-1)H_2O \qquad (15)$$

$$nCH_4 \longrightarrow C_nH_{2n+2} + (n-1)H_2 \qquad (16)$$

We observed methane reacts at a lower temperature. Using Ru_4ZL as catalyst, 2.25% of methane reacted at 200°C, producing mainly hydrogen and carbon dioxide. C_2 hydrocarbons are produced at 400°C or higher temperature. The methane conversion is much higher when compared to the direct coupling reactions (Table 3. Unfortunately, most of the reacted methane is converted to carbon dioxide and water. The selectivity of C_2 hydrocarbon is low, indicating the noncatalytic gas phase oxidation is a problem in this reaction. Also, these reactions produce significant amounts of hydrogen, which were not expected based on equations (8) and (9). This result suggested the methane reacts by a direct coupling path [equation (16)] after the input oxygen has consumed. The advantage of this approach is high conversion at low temperature but the selectivity of C_2 hydrocarbon needs to be improved.

Table 3

OXIDATIVE COUPLING OF METHANE OVER Ru_4ZL[a]

Temperature (°C)	CH_4 Conversion (%)[c]	Selectivity to[b]		
		H_2(%)	CO_2(%)	C_2(%)
200	2.26	16.30	2.33	--[d]
300	3.47	10.61	24.52	--
400	18.87	30.71	61.61	0.44
500	21.09	31.81	54.04	2.32

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[a] Reaction conditions: pressure = 50 psig; flow rate = 10 mL/min; CH_4/O_2 = 10.

[b] Selectivities to hydrocarbons are based on carbon number and the amount of methane reacted.

[c] Data are based on four continuous runs within a 1-hour period.

[d] Not detected.

In summary, our results how that these organometallic-derived ruthenium clusters are effective in reforming methane. The methane conversion ranges from 1.74 to 10.11%. They are much lower than the commercial ruthenium catalyst. However, the commercial ruthenium catalyst produces only trace amounts of C_2 hydrocarbon and no higher hydrocarbons, apparently forming coke. Therefore, the commercial catalyst is not useful for our purpose. Our ruthenium catalysts produce considerable higher hydrocarbons, C_2 and C_6 or higher. A very small amount of CO_2 is also produced in these reactions and is probably due to the impurity (e.g., oxygen) in the gas cylinder.

Most of the reports on catalytic conversion of methane to higher hydrocarbons are based on metal oxides by the oxidative coupling pathway. Few examples have been reported on direct methane reforming. Table 4 lists some of the literature results on both oxidative coupling and reforming together with our results. It is difficult to truly compare the catalytic activities of the catalysts because the experimental conditions are so different. However, based on the methane convention and the selectivities of higher hydrocarbons, our catalysts are comparable. We believe the catalytic activities of our ruthenium catalysts can be improved by proper modification of the reaction conditions. Generally speaking, the oxidative coupling of methane gives only C_2 hydrocarbons, but the methane reforming gives higher molecular weight hydrocarbons (C_6+) in addition to the C_2 hydrocarbons. None or very small amounts of C_3-C_5 hydrocarbons have been detected. Mitchell and Waghorne[51] reported the major product of alumina-supported CaCrPt catalyst under anaerobic condition is benzene. Jones et al.[52] also observed small amounts of benzene produced from the methane reforming over silicon-supported GeO_2. We have not yet identified our C_6+ product, but it is possible that it contains benzene.

Table 4

COMPARISON OF THE ACTIVITIES OF CATALYSTS FOR METHANE POLYMERIZATION

Catalyst	CH_4/O_2	Temp. (°C)	Pressure (atm)	GHSV (hr^{-1})	CH_4 Conversion (%)	Selectivity to		Ref. No.
						C_2(%)	C_6+(%)	
Li/MgO	2	720	1	2754	37.8	50.3	N.R.[a]	1
CacrPt/γAl_2O_3	>200[b]	705	1	N.R.	27.64[c]	31.4	68.3[d]	2
PbO/MgO	6	750	1	8000	10.0	65.5	N.R.	3
Sm_2O_3	6	750	1	3.8×10^7	6.5	60.0	N.R.	4
Ru_6AL	>200	750	4.5	16000	6.06	6.9	41.4	this work
Ru_6ZL	>200	750	18.5	32000	2.62	9.2	20.6	this work
Ru_4ZL	>200	750	4.5	16000	1.74	6.9	28.9	this work
Sb_2O_3/SiO_2	>200	800	1	600	0.25[b]	82.9	—	5
GeO_2/SiO_2	>200	700	1	860	0.22	57.1	3.3[d]	6

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[a] Not reported.
[b] Cumulative result.
[c] No added oxygen.
[d] Benzene.

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FUTURE WORK

Our ruthenium catalysts are catalytically active in reforming methane. We will try to improve both the methane conversion and the product yield by optimizating the reaction conditions and nature of the catalyst. The correlation between the cluster size and the pore size of support material will be further studied. We will also modify our analytical method for the heavy hydrocarbon to obtain a better understanding of the product distribution. Another approach to improve the product yield is to control the partial pressure of hydrogen (Phase 2 of Task 2). We will begin to build a reactor that includes a palladium membrane as shown in Figure 1.

During the next reporting period, we will spend more of our effort on Task 4. We have synthesized some zeolite encapsulates phthalocyanine metal complexes. Initial tests show that the ruthenium phthalocyanine complex has some catalytical activity in partial oxidation of methane to methanol. We will use the reactor system to quantitatively monitor this reaction.

EXPERIMENTAL DETAILS

A schematic representation of the reactor sysytem is shown in Figure 1. The system has five gas inlet ports: one each for methane and oxygen, one for helium purge, one for hydrogen (which can be used to reduce catalyst), and one spare inlet port for a reaction initiator such as ethane. The gases are filtered through a 1-μm in line filter, after which they pass through a vented inlet system controlled by a three-way valve. This inlet arrangement allows for changes in the feed gas composition without having to shut down the reactor system.

The gas flows are controlled by mass flow controllers. Check valves are installed after the mass flow controllers to prevent back flow. The pressure of the gas mixture is indicated by a pressure gauge and a pressure transducer. An adjustable pressure relief valve is corrected to the reactor effluent line. A vacuum line is also connected for activating the catalyst and for removing air in the system after a change of catalyst. The reactor is equipped with quick connects on both ends to allow rapid change of catalyst without exposure to air and a thermocouple immersed in the catalyst bed for temperature control. The outlet gas from the reactor is led through a back pressure regulator, a pressure gauge, and a needle control valve that is used to control the flow rate. The gas is then introduced to the gas sampling valves inside the Carle 500 GC and then vented through a oil bubbler and a soap-film flowmeter. The bubbler prevents any back diffusion of air and serves as a flow indicator.

The maximum operating pressure of this system is 250 psi, which is limited by the quick connects and the back pressure regulator. A higher pressure limit can be achieved by simple replacement of those components if desired at a later stage of the project.

General Procedure for Testing Methane Reforming Catalysts

The catalyst (500 mg) is loaded into the stainless steel reactor (0.22 inch ID) under an inert atmosphere. The reactor is connected to the reactor system and purged with helium for 15 min. A helium diluted methane gas (contains about 20% methane) is introduced at 150 psig through a mass flow controller to the reactor. The back pressure is set at 50 psig and the methane flow rate is controlled by the mass flow controller. A thermocouple is immersed in the catalyst bed and connected to a temperature controller, which controls the furnance. The outlet gases are fed to a Carle 500 gas chromatograph for sample analysis. The GC is programmed to separate light gases including hydrogen and hydrocarbons up to C_5. The C_6 or higher hydrocarbons and other polar compounds (C_6+) are back flushed from the column to the detector. The calibration of C_6+ is based on the area integration and referenced to the methane peak. Other components are calibrated with standard sample mixtures. Initial methane concentration is measured before and after each run at ambient temperature under the same pressure and flow rate.

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