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DIRECT CATALYTIC CONVERSION OF METHANE AND LIGHT HYDROCARBON GASES

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INTRODUCTION AND SUMMARY

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.

In our second quarterly report, we presented the test results of six methane reforming catalysts that were prepared by "surface-confining" ruthenium clusters. The effect of cluster size, support material, and reaction conditions were evaluated. The methane conversions ranged from 1.74 to 10.1% at 750°C. The reaction product contains hydrogen, C_2 hydrocarbons, and C6 or higher hydrocarbons. Up to 48.34% yield of hydrocarbon is obtained based on reacted methane. Some of these catalysts show good coking resistance compared with a commercial ruthenium catalyst. Addition of oxygen to these reactions significantly increases the methane conversion at lower temperature; however, carbon dioxide and water become the major products.

During this reporting period, we concentrated on synthesizing and testing methane oxidation catalysts using the automated GC sampling system. We modified our preparation method of zeolite-encapsulated phthalocyanines (PC). The catalysts have higher complex loading, and the uncomplexed metal ions were back-exchanged by sodium ions (to remove any uncomplexed metal ions). Four metal ions were used: cobalt, iron, ruthenium, and manganese. We also synthesized four zeolite-encapsulated tetraphenylporphyrin (TPP) complexes using the same metals. These catalysts were tested for methane oxidation in the temperature range from 300° to 500°C at 50 psig pressure. The RuPC, CoTPP, and MnTPP showed activity toward the formation of methanol. The RuPC zeolite gave the best methanol yield. The methane conversion was 4.8%, and the selectivity to methanol is 11.3% at 375°C. Again, the major products are carbon dioxide and water in every catalyst we tested during this reporting period.

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

Our approach in Task 1 is to synthesize methane-reforming catalysts by thermally decomposing surface-confined metal clusters of carefully controlled size. The variables we are studying include cluster size, cluster composition, and activation procedures. The support materials are zeolites and rare-earth-exchanged zeolites; the metal complexes are the low-valent complexes of Re, Fe, Ru, Rh, and/or their mixtures. Clusters of 2-4 metal atoms are used as catalyst precursors with an emphasis on Re and Ru.

Research is under way* on the technique 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 are studying 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 began with the following compounds: For Re, we are using $Re_2(CH_2SiMe_3)$ 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 are 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 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 are testing the methane-reforming catalysts in two phases. Phase 1 consists 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.

The Phase 1 experiments are conducted in a fixed-bed isothermal microreactor in a down-flow mode at atmospheric pressure. An automated Carle two-column GC is used to follow the conversion of methane and

product formation. Variables include space velocity and temperature. A commercially available platinum-based reforming catalyst (such as the Chevron catalyst) is 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.

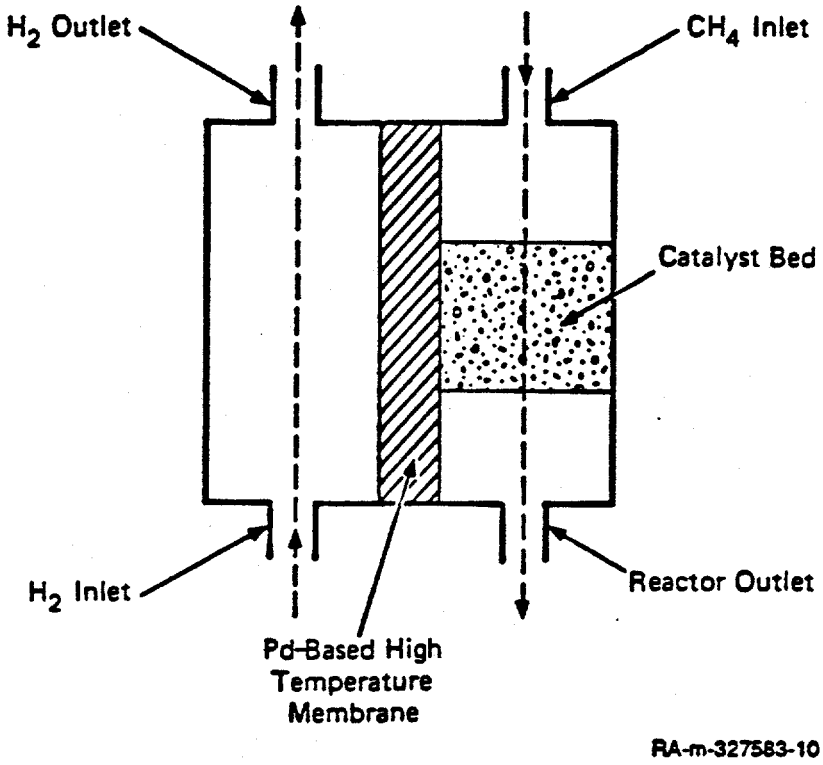
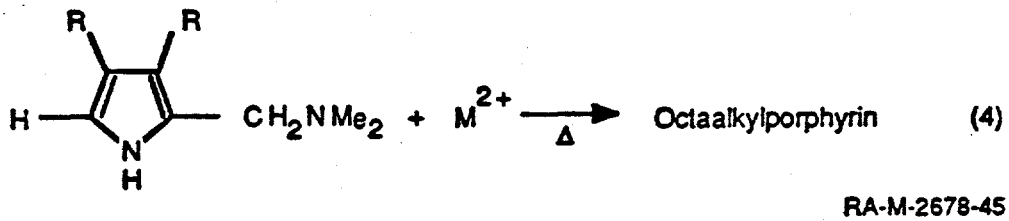


FIGURE 1 SCHEMATIC OF REACTOR WITH MEMBRANE FOR HYDROGEN CONTROL

Task 3: Synthesis of Oxidation Catalysts for Methane

In Task 3, we are synthesizing oxidation catalysts by encapsulating porphyrin and phthalocyanine metal complexes in zeolites. Variables include the porphyrin or phthalocyanine ligand, the type of metal, and the type of zeolite. The metal complexes used are Cr, Mn, Re, Ru, and/or Co, with emphasis on the Ru examples.

The porphyrin and phthalocyanine complexes are 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)] gives the desired porphyrin.



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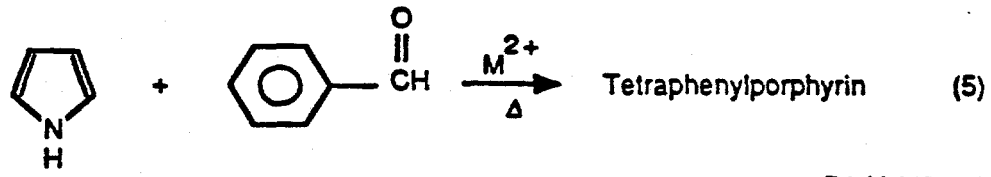
Alternatively, the cocondensation of pyrrole with benzaldehyde gives tetraphenylporphyrin [equation (5)].[30]



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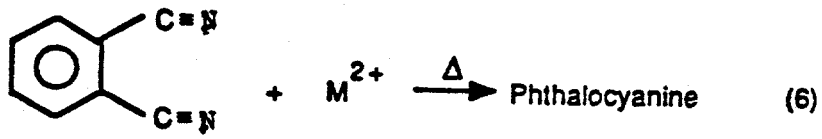
The phthalocyanines are produced by the condensation of phthalonitriles [equation (6)].



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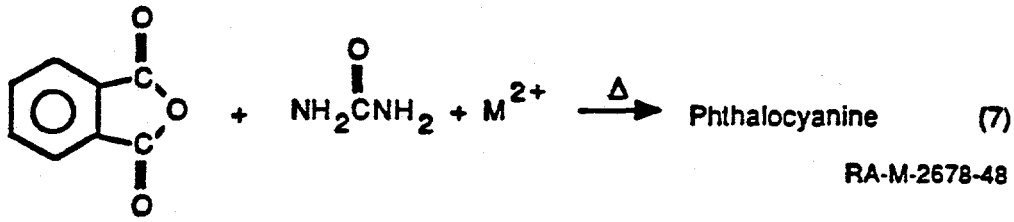
Alternatively, the condensation of phthalic anhydride and urea produces phthalocyanine [equation (7)].[31]



Task 4: Testing of Methane Oxidation Catalysts

The objective of Task 4 is to test methane oxidation catalysts in the same fixed-bed isothermal down-flow reactor used in Task 2. We are using an automated two-column GC to follow the conversion of methane and oxygen and product formation. Low oxygen concentrations were used initially and the variables include space velocity, temperature, and feed composition. For comparison, we are also using a commercially available oxidation catalyst, such as an bismuthmolybdate catalyst (Sohio) or vanadium pentoxide (American Cyanamid). Finally, we are investigating mixtures of light hydrocarbons.

General Methods

The reactions are conducted in the fixed-bed isothermal micro-reactor described above.[32-34] The exhaust gases from the reactor are 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 are 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 are thus 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 is therefore measured by three independent methods.

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

The oxidation state(s) of the confined metal catalysts is determined using Auger and/or ESR spectroscopy.

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

RESULTS AND DISCUSSION

Our first approach to the development of methane reforming catalysts concentrated on surface-confined ruthenium clusters. Highly dispersed tetraruthenium and hexaruthenium clusters were supported on alumina, 5A molecule sieve, and Y-zeolite. All catalysts showed activity in reforming methane. The syntheses and test results were reported in the previous quarterly report. We analyzed the carbon contents in the reacted catalysts and found that some of these catalysts have good resistance to coking. The relation between catalyst location in the support and coke formation is discussed in the following section.

During this reporting period, we continued to synthesize and test methane oxidation catalysts. The preparation method and catalyst purification method were improved. We tested eight zeolite-encapsulated phthalocyanine (PC) and tetraphenylporphyrin (TPP) complexes of cobalt, iron, ruthenium, and manganese. The RuPC, CoTPP, and MnTPP showed some selectivity toward the formation of methanol. Other catalysts gave carbon dioxide and water.

Task 1: Synthesis of Advanced Reforming Catalysts for Methane

The results of this task are described in Quarterly Report No. 2.

Task 2: Testing of Methane Reforming Catalysts

During the previous reporting period, we tested six ruthenium catalysts for methane reforming. These catalysts are Ru_4 and Ru_6 clusters supported on three supports: alumina (AL), 5A molecular sieve (MS), and Y-zeolite (ZL). The location of the cluster on or within the support depends on the sizes of the cluster molecule and the cage of the support. We predicted that the Ru_4 will be confined inside the pores of molecular sieve and zeolite, whereas the larger cluster Ru_6 will enter

only inside the zeolite cage. The elemental analyses listed in Table 1 indirectly support our prediction. The catalysts dispersed on the support surface promote coke formation, as noted from the large increases in carbon content of the Ru_4AL, Ru_4MS, and Ru_6AL after reaction with methane. In contrast, the carbon content in Ru_4ZL and Ru_6ZL decreases after reaction, which suggests that coking of these catalysts is not observed and the decrease in carbon content is due to the decomposition of the ruthenium complexes, that is, the release of carbon monoxide. The carbon content in Ru_4MS increases slightly after reaction with pure methane, but decreases after reaction with a methane/oxygen mixture. Therefore, adding oxygen to the methane reforming reaction not only changes the reaction mechanism (as evidenced by a change in product distribution) but also eliminates the coking problem.

Table 1

ELEMENTAL ANALYSES OF RUTHENIUM CATALYSIS FOR METHANE REFORMING[a]

	Before Reaction			After Reaction		
	%C	%H	%Ru	%C	%H	%Ru
Ru_4AL	5.09	1.04	0.61	26.50	0.40	0.57
Ru_4MS	1.46	1.13	0.49	4.38	0.46	0.64
Ru_4MS[b]				0.32	0.35	1.00
Ru_4ZL	5.25	1.53	0.61	0.58	0.22	1.26
Ru_6AL	9.77	1.84	1.26	23.24	0.67	0.55
Ru_6MS	0.95	1.68	0.19	22.29	0.19	0.32

[a]Reaction with pure methane at 750°C.
[b]Reaction with methane/oxygen (10:1) at 500°C.

Interestingly, the hydrogen content of all catalysts decreases after reaction with methane. Although the ruthenium complexes contain

some hydrogens in the form of hydride or unreacted alkyl groups, but the hydrogen decrease is too large to be accounted for from the metal complexes alone. This result suggests that the hydrogen in the original supports, for example, acidic protons, is consumed during reaction. It is not clear whether the supports are used during the catalytic reaction or simply removed by the heating process.

We also observed variations in the ruthenium content of these catalysts before and after reaction. The results are inconsistent probably because of the experimental error of the difficult analytical method for Ru in solids.

Task 3: Synthesis of Oxidation Catalysts for Methane

Our synthesis strategy for methane oxidation catalysts is to encapsulate the metal ion into the zeolite support using an ion exchange method and then to use a metal ion template reaction to synthesize the metal complex within the zeolite cage. During the first quarter of this program, we synthesized three zeolite-encapsulated phthalocyanine (PC) complexes: FePC, CoPC, and RuPC. We found that some of the metallophthalocyanines are absorbed on the zeolite surface instead of inside the zeolite cage. Therefore, we washed the catalysts with pyridine using a Soxhlet extractor until the pyridine solution was clear. The elemental analysis results show that washing the catalyst significantly decreases the carbon and the metal contents, particularly for the FePC and the RuPC (Table 2).

During this third quarter we synthesized another batch of phthalocyanine catalysts with higher complex loading. It is known that a loading of 2.4% Fe corresponds to approximately one complex per supercage of the zeolite.[1] We attempted to prepare zeolite-encapsulated complexes with this maximum metal loading. The elemental analysis results shown in Table 3 indicate that the CoPCZL contains approximately one complex per zeolite cage. The carbon and nitrogen analyses are in good agreement with the theoretical calculation. The hydrogen content is higher than the theoretical calculation because of the acidic protons

in the zeolite structure. The FePCZL and the MnPCZL contain approximately two complexes for every three cages.

Table 2

ELEMENTAL ANALYSES OF METHANE OXIDATION CATALYSTS
BEFORE AND AFTER WASHING

	Before Washing			After Washing with Pyridine		
	%C	%H	%Metal	%C	%H	%Metal
CoPC	14.53	1.59	1.96	2.45	1.66	1.81
FePC	25.61	1.80	1.19	5.95	2.45	0.85
RuPC	17.35	1.87	1.58	7.16	2.06	0.40

Table 3

ELEMENTAL ANALYSES OF METHANE OXIDATION CATALYSTS
WITH INCREASED COMPLEX LOADING

	Experimental				Theoretical[a]			
	%C	%H	%N	%M	%C	%H	%N	%M
CoPCZL	14.49	2.56	4.49	2.56	14.58	0.62	4.25	2.23
	14.67	2.60	4.48	2.52				
FePCZL	11.46	1.79	3.04	4.08	11.47	0.48	3.34	1.67
	11.48	1.65	3.12	4.02				
MnPCZL	10.50	2.06	2.75	2.74	10.49	0.43	3.05	1.50
	10.48	2.03	2.72	2.77				
CoTPPZL	3.93	2.24	1.26	2.21	3.92	0.22	0.39	0.39
	3.91	2.13	1.31	2.18				
FeTPPZL	3.66	2.43	1.29	3.82	3.66	0.21	0.39	0.39
	3.65	2.30	1.28	3.90				
RuTPPZL	3.44	2.09	0.69	0.27	3.31	0.19	0.35	0.63
	3.17	2.03	0.71	0.24				

[a]Calculated based on carbon content.

Free metal ions also exist in these PC zeolites. To test the true catalytic activity of the zeolite-caged-metal complexes, we need to remove the excess metal ions. Thus, the free metal ions in every catalysts prepared are back-exchanged with sodium ion by stirring in sodium chloride solution at room temperature. The results of the elemental analyses listed in Table 4 indicate that the reverse ion exchanges are successful for Co and Mn but not for Fe. Both of the FePC and FeTPP zeolites contain approximately the same percentage of iron before and after the sodium ion exchange process. The RuPCZL and the RuTPPZL are similar to the iron catalysts in that the ruthenium content remains the same within experimental error.

Table 4

ELEMENTAL ANALYSIS OF METHANE OXIDATION CATALYSTS
BEFORE AND AFTER SODIUM ION EXCHANGE

Catalyst[a]	% Carbon	% Hydrogen	% Nitrogen	% Metal
CoPCZL	14.49	2.56	4.49	2.56
CoPCZL[b]	12.14	1.43	3.43	1.53
FePCZL	11.46	1.79	3.04	4.08
FePCZL[b]	8.06	1.51	1.98	4.15
RuPCZL	4.64	2.51	0.64	0.82
RuPCZL[b]	2.30	1.68	0.42	0.97
MnPCZL	10.50	2.06	2.75	2.74
MnPCZL[b]	9.31	1.42	2.39	1.62
CoTPPZL	3.93	2.24	1.29	3.83
CoTPPZL[b]	2.36	1.01	0.41	0.15
FeTPPZL	3.66	2.43	1.29	3.83
FeTPPZL[b]	2.36	1.04	0.48	4.04
RuTPPZL	3.44	2.09	0.69	0.27
RuTPPZL[b]	2.46	1.13	0.52	0.13
MnTPPZL	8.33	2.24	1.03	1.42
MnTPPZL[b]	4.96	1.22	0.58	0.12

[a]PC = phthalocyanine, TPP = tetraphenylporphyrin, ZI = zeolite.
[b]After sodium ion exchange.

Our first attempt to synthesize another type of zeolite-encapsulated metal complex, the metalloporphyrins, was unsuccessful. Reaction of benzaldehyde, pyrrol, and metal-exchanged zeolite in refluxing dimethylsulfoxide does not give the desired product. Obviously, the template synthesis of phthalocyanine does not work for porphyrins. We then tried another route to synthesize the metal-free ligand inside the zeolite cage first by refluxing benzaldehyde, pyrrol, and the sodium zeolite (without metal exchange) in acetic acid. The resulting zeolite powder, after being washed with methanol, turned purple, which indicated the formation of the porphyrin. The wash contained tetraphenylporphyrin as indicated by its UV-VIS spectrum.

The desired metal ion was inserted into the porphyrin by boiling the metal salt and the zeolite containing the porphyrin in dimethylsulfoxide solution. The product was washed with water and then Soxhlet extracted with methanol to remove surface-bound TPP complex. Uncomplexed metal ions are removed by reverse ion-exchange. Four metal complexes, Co, Fe, Ru, and Mn, were prepared during this period. The percent complex loading of these porphyrin catalysts is much lower than those of phthalocyanine catalysts. The main reason may be the low yield of ligand synthesis, which is generally about 20%.

Task 4: Testing of Oxidation Catalysts

We tested all eight zeolite catalysts that were treated with sodium ion for methane oxidation at 375°C under 50 psig pressure. We used the same reactor system as in Task 2. A heated 1/16-inch-diameter stainless steel tube (110°C) was added between the reactor and the GC sampling valve. The methane-to-oxygen feed ratio was 4 and the GHSV (gram hourly space velocity) was about 2600 h^{-1}. Catalysts were activated under hydrogen flow at 200°C for 2 h before the methane/oxygen mixture was introduced. Thus, the Fe(III) complexes are reduced to Fe(II). When synthesized with $Ru_3(CO)_{12}$, the Ru complexes obtained were coordinated with CO. Activation with hydrogen reductively removed the CO and freed the coordinate site. Other impurities, such as water and residual solvent, were also removed during this process.

The methane reaction results are averaged from data taken from a 15- to 20-h run with GC samples analyzed every hour and are summarized in Table 5. Three catalysts, RuPCZL, CoTPPZL, and MnTPPZL, showed some activity toward the formation of methanol. As shown in Table 5, the RuPcZL gave the highest selectivity for methanol. The methane conversions were generally below 10%. Carbon dioxide and water were always the major products.

Table 5

ACTIVITY OF METHANE OXIDATION CATALYSTS[a] AT 375°C

	% Conversion		% Selectivity		
Catalyst	CH_4	H_2	CO_2	H_2O	CH_3OH
Zeolite	0.5	---	100	---	---
RuZL	15.9	45	100	100	---
RuTCPC	1.7	---	100	206	---
CoPCZL	6.3	---	100	100	---
FePCZL	18.2	1.2	100	42	---
RuPCZl	4.8	---	87	1	11.3
MnPCZL	9.6	---	80	65	---
CoTPPZL	1.9	---	94	120	5.8
FeTPPZL	1.9	---	100	73	---
RuTPPZL	8.4	50	99	146	---
MnTPPZL	1.8	---	95	126	3.5

[a]Reaction conditions: temperature = 375°C, pressure = 50 psig, CH_4/O_2 = 4, GHSV = 2600 h^{-1}.

Three control experiments were performed using the blank zeolite, the ruthenium-exchanged zeolite (with triruthenium dodecacarbonyl), and the ruthenium tetracarboxyphthalocyanine. The blank zeolite gave essentially no activity for methane oxidation. Less than 0.5% of methane was oxidized to carbon dioxide. The ruthenium zeolite produced hydrogen, carbon dioxide, and water with approximate 16% methane

conversion. The RuTPPZL and FePCZL also produced hydrogen, which suggests that these two catalysts behave like the simple metal-exchanged zeolite because the excess metal ion in these two catalysts were not removed by the reverse ion exchange process. Hydrogen was produced as a result of the catalytic ability of the metal particles within the zeolite. We obtained similar results with the ruthenium cluster bonded zeolite. At 400°C and a CH_4/O_2 ratio of 10, Ru_4ZL gave 30.7% of hydrogen and 61.6% of carbon dioxide with 18.9% methane conversion. These results were presented in the previous quarterly report.

In the absence of zeolite support, RuTCPC does not convert methane to the desired product. Only 1.7% of methane was consumed, and the products were carbon dioxide and water. A slight excess of water was produced due to the decomposition of the peripheral substituent (-COOH). TCPC was chosen simply because of its availability in our laboratory.

Some of the catalysts were also tested at a higher temperature (450°-500°C) under otherwise identical conditions. The results were averaged from 4-h runs and are summarized in Table 6. Methane conversions were generally increased. Again, only RuPCZL and CoPCZL showed any activity toward methanol formation, but the yields decreased significantly. These results suggest that the reactions at the lower temperature (375°C) produce higher yields. Also at high temperature, the ligands decomposed.

Table 7 lists the elemental analysis results for the catalysts after reaction with methane and oxygen at 450°C. The carbon contents decreased to less than 0.2% except for the RuTPPZL which remained approximately the same. RuTPP may be more stable than the other complexes. With CoPCZL, we observed a mixture of hydrocarbons released during the first hour of reaction at 375°C.

The ligand decomposition at higher temperature indicates that our previous test results on the RuPCZL were possibly incorrect. We reported in the eighth monthly report that the crude RuPCZL gave C_2 and C_3 hydrocarbon products during 2- to 4-h runs in the temperature range of 300° to 500°C. These hydrocarbons might result from the decomposition of the ligand rather than true products. Further investigation is under way.

Table 6

ACTIVITY OF METHANE OXIDATION CATALYSTS AT LOW (375°C) AND HIGH (450°C-500°C) TEMPERATURES[a]

Catalyst	Temp (°C)	% Conversion		Selectivity			
		CH_4	O_2	H_2	CO	H_2O	CH_3OH
RuZL	375	15.9	99.0	45.0	100.0	100.0	---
	500	20.8	99.0	110.0	89.3	---	---
FePCZL	375	18.2	53.9	1.2	100.0	42.5	0.0
	500	22.7	87.2	15.9	100.0	45.0	---
RuPCZL	375	4.8	14.5	---	87.5	0.5	11.3
	450	9.0	99.6	---	96.7	0.5	3.3
CoTPPZL	375	1.9	15.1	---	94.3	119.7	5.8
	450	3.3	56.1	---	98.0	126.2	2.0
FeTPPZL	375	1.9	15.1	---	100.0	---	---
	450	6.1	32.8	---	100.0	65.1	---

[a]Reaction conditions: pressure = 50 psig, CH_4/O_2 = 4, GHSV = 2600 h^{-1}.

Table 7

ELEMENTAL ANALYSIS OF METHANE OXIDATION CATALYSTS AFTER REACTION WITH METHANE AND OXYGEN AT 450°C

Catalyst[a]	% Carbon	% Hydrogen	% Nitrogen	% Metal
FePCZL[b]	8.06	1.51	1.98	4.15
FePCZL[c]	0.10	0.46	<0.05	3.46
RuPCZL[b]	2.30	1.68	0.42	0.97
RuPCZL[c]	0.13	1.00	0.10	0.89
CoTPPZL[b]	2.36	1.01	0.41	0.15
CoTPPZL[c]	0.19	0.47	0.26	0.20
FeTPPZL[b]	2.36	1.04	0.48	4.04
FeTPPZL[c]	0.20	0.69	<0.10	4.03
RuTPPZL[b]	2.46	1.13	0.52	0.13
RuTPPZL[c]	2.13	0.99	0.32	0.14

[a]PC = phthalocyanine, TPP = tetraphenylporphyrin, ZL = zeolite.
[b]Before reaction.
[c]After reaction of methane and oxygen at 450°C.

FUTURE WORK

The stability of the promising oxidation catalysts will be a key subject for future study. We will measure their decomposition point by TGA. The activity of the catalysts will be measured at temperatures below their decomposition point. The selectivity to methanol and the methane conversion could be improved under optimum reaction conditions, which include the methane-to-oxygen ratio, pressure, flow rate, and the amount of complex loading. Another important factor is the axial ligand effect. Our catalysts were treated with pyridine during the preparation; another axial base, such as imidazole, may be a better ligand for oxygen activation.

We have begun to synthesize other macrocyclic metal complexes, including tetramesitylporphyrin and Schiff base complexes. The ruthenium tetramesitylporphyrin has been shown to transfer molcular oxygen to organic substrate in a homogeneous system.[49] We will also test other metal ions such as chromium and rhenium.

During the next reporting period we will synthesize and test monoruthenium catalysts for methane reforming. A new reactor equipped with an in-situ Pd membrane to control the hydrogen partial pressure will be assembled. Selected catalysts will be tested using this reactor. Future work will include the synthesis and testing of mixed-metal cluster catalysts.

EXPERIMENTAL DETAILS

Preparation of Metal Ion Exchanged Zeolite

To a slurry of 500 g zeolite (LZ-Y52, Union carbide) and water (500 mL), a 1 M aqueous solution of metal salt [500 mL, $FeCl_2$, $CoCl_2$, $MnSO_4$, or $Ru(DMSO)_2Cl_2$] was added dropwise. The zeolite slurry was stirred at a constant speed. The total addition time was approximately 1 h. The mixture stirred for 24 h. The exchanged powder was filtered, washed with water until the solution was free of chloride or sulfate, and then dried at 150°C under vacuum for 48 h. Elemental analysis of Co-zeolite: C, 0.27; H, 0.91; Co, 4.76; Fe-zeolite: C, 0.26; H, 1.20; Fe, 4.89; Ru-zeolite: C, 1.16; H, 1.08, Ru, 0.95.

Preparation of Zeolite-Encapsulated Metallophthalocyanine

Metal-exchanged zeolite (100 g) and 8 equivalents of 1,2-dicyanobenzene were added to 200 mL of nitrobenzene in a round-bottom flask fitted with a reflux condenser and a mechanical stirrer. The mixture was heated to 180°C for 4 h under nitrogen until the solution changed color (dark green for Fe, dark blue for Co, brown for Mn and Ru). The zeolite was filtered, washed with methanol to remove nitrobenzene, and Soxhlet extracted with pyridine until the solution was clear. Excess pyridine was removed by Soxhlet extraction with methanol. The zeolite powder was then boiled in a 1 M solution of NaCl (reverse metal exchange) for 4 h, and washed with water and acetone. The product was dried at 150°C under vacuum for 24 h.

Preparation of Zeolite-Encapsulated Tetraphenylporphyrin

Zeolite powder (200 g) was added to 1.8 L of acetic acid in a 2-L round-bottom flask equipped with mechanical stirrer and an additional funnel that contained 46.5 mL of pyrrol and 66.5 mL of benzaldehyde. The acetic acid was heated to boil. The pyrrol and benzaldehyde were

added slowly. The reaction mixture was boiled for 0.5 h under air. The dark purple solid was filtered while the solution was still warm. It was then washed with a large amount of acetone until the solution was clear. The product was dried at 150°C under vacuum for 24 h.

Metal Insertion of Tetraphenylporphyrin in Zeolite

A mixture of TPP zeolite (50 g) and metal salt [0.12 mole of $CoCl_2$, $FeCl_2$, $MnSO_4$, or $Ru_3(CO)_{12}$] was added to 200 mL of dimethyl sulfoxide in a three-necked round-bottom flask equipped with a mechanical stirrer, a reflux condenser, and a gas inlet adaptor. The reaction mixture was heated to reflux for 3 h. The product was washed with water and methanol. Excess metal salt was removed by boiling in a 1 M aqueous solution of NaCl for 2 h. The product was washed again with water and methanol and then dried at 150°C for 24 h.

General Procedure for Testing Methane Oxidation Catalysts

The catalyst (3 g) was loaded into a stainless steel reactor (3/8 inch OD). The reactor was connected to the reactor system and purged with helium for 15 min. It was heated to 200°C under a slow flow of hydrogen for 2 h. Methane (10.3% in helium) and oxygen (5.2% in helium) were introduced to the reactor, and the temperature was increased to 300°C or higher. Methane and oxygen were individually controlled by mass flow controller. Reactor pressure was set at 50 psig by a back pressure regulator. A thermocouple was immersed in the catalyst bed and connected to the temperature controller that controls the furnace. The outlet gases were fed to a GC sampling value through a heated stainless steel tube (110°C).

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