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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 gasifier² 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 this reporting period, we concentrated on Tasks 1 and 2, the methane reforming reactions. We synthesized three monomeric ruthenium catalysts and tested their activities. They gave high yields of hydrogen, similar to the ruthenium clusters. The methane conversion and the selectivities to C2 hydrocarbons were both less than 3%.

We attempted to drive the reaction equilibrium toward product formation by removing the hydrogen from the catalyst bed. We built a new reactor that contained a Pd/Ag membrane tube inside the reactor. Hydrogen formed in the reactor will diffuse into the Pd/Ag tube and be removed either by vacuum or by helium flow. We encountered some difficulty in handling the fragile Pd/Ag membrane tube. Nevertheless, we tested two of our catalysts by this method, but the results were not encouraging. We suspect that the reaction was not reaching equilibrium because of the high flow rate. Since these results were significantly different than those observed previously with Pd/Ag membrane, in which significant product distributions were observed, it is likely that the reactor configuration plays an important role.

Thus, we studied the effect of flow rate on the reforming reaction without using the Pd/Ag memberane. We found that methane conversion was higher at lower flow rates. When 5 g of Ru₄ZL was used at a flow rate of 50 mL/min in a 1/4-in. reactor, the methane conversion was 43% at 750°C and 150 psig pressure. The product selectivity was unchanged by flow rate.

We began synthesizing mixed-metal catalysts for methane reforming. A FeRu₃ cluster was synthesized and anchored on Y-zeolite using the same method that was used for preparing the ruthenium cluster catalysts.

We also examined another type of support, magnesia. The basicity of this support seems advantageous to the methane reforming.

In addition, we continued to synthesize oxidation catalysts and prepared a zeolite-encapsulated ruthenium tetramesitylporphyrin. Syntheses of other metal complexes are under way.

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

*SRI's study of the techniques for HDN catalysis, DOE Contract No. DE-FG-22-85PC80906, 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)].

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 $Re_2(CH_2SiMe_3)_2$ 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, $Rh_2(2\text{-hydroxy-6-methylpyridine})$. Clusters are prepared from the hydridocarbonyl clusters by relying on reactions such as (2) and (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

We 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 pressure²⁸ (see Figure 1). Variables to be studied will also include space velocity of methane, temperature, hydrogen pressure, and hydrogen flow rate.

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.

RA-m-327583-10

FIGURE 1 SCHEMATIC OF REACTOR WITH MEMBRANE FOR HYDROGEN CONTROL

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.

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

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

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

RA-M-2678-48

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 a bismuthmolybdate catalyst (Sohio) or vanadium pentoxide (American Cyanamid). Finally, we are investigating mixtures of light hydrocarbons.

RESULTS AND DISCUSSION

During this quarter, we synthesized five new catalysts, including a monomeric ruthenium complex and a mixed cluster of iron and ruthenium. In addition to the three acidic supports we have used (alumina (AL), 5A molecular sieve (MC), and Y-zeolite (ZL), this quarter we tested a basic support, magnesia. In tests of the activity for methane reforming, the monomeric ruthenium catalysts gave high yields of hydrogen, similar to the ruthenium clusters we tested before. Methane conversion and hydrocarbon selectivities are slightly lower than for the clusters. The magnesia-supported Ru_4 cluster showed higher selectivity to hydrocarbon production but methane conversion was lower.

Removing hydrogen from the methane-reforming reaction will increase methane conversion by forcing the reaction equilibrium toward products. During this reporting period, we built a new reactor that contained a Pd/Ag membrane tube to remove hydrogen from the catalyst bed. We tested two catalysts, Ru_6AL and Ru_4ZL . The methane conversion did not increase in either test. These reactions may not have reached equilibrium under our reaction conditions, particularly because of the high flow rate.

We studied the effect of space velocity by varying the flow rate and by increasing the amount of catalyst used. The results showed that decreasing the space velocity generally increases the methane conversion. The production of hydrogen was also increased. However, the change of space velocity did not alter the product selectivity.

We also started the synthesis of a new methane oxidation catalyst by incorporating tetramesitylporphyrin into the zeolite supercage. The metal ion was subsequently inserted into the center of the macrocyclic ligand.

Task 1: Synthesis of Advanced Reforming Catalysts for Methane

We have synthesized a monomeric ruthenium complex and a mixed metal cluster of iron and ruthenium. The monomeric ruthenium complex,

$\text{Ru}(\text{Allyl})_2(\text{CO})_2$, was synthesized by surface confinement techniques according to a method developed in our laboratory on another research project.³² Alumina, 5A molecular sieve, and Y zeolite were used as supports. $\text{Ru}(\text{Allyl})_2(\text{CO})_2$ reacted with the surface hydroxy group of the support to give highly dispersed ruthenium catalysts. The metal loadings were 0.35% on alumina, 0.37% on 5A molecular sieve, and 0.37% on zeolite.

A mixed metal cluster of iron and ruthenium was synthesized by reacting $\text{Na}_2[\text{Fe}(\text{CO})_4]$ and $\text{Ru}_3(\text{CO})_{12}$ in THF.³³ Subsequent acidification with H_3PO_4 gave $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$. The product was separated by column chromatography and crystallized from hexane. The product was identified by its infrared spectrum. This compound is redissolved in hexane and reacted with triethyl aluminum.

The amount of ethane evolved from the reaction was measured and was equal to one equivalent of ethane per metal cluster. This result is consistent with our experience with the ruthenium clusters in which only one of the acidic protons reacted with $\text{Al}(\text{C}_2\text{H}_5)_3$. The aluminum bonded cluster is dissolved in THF and reacted with the hydroxy group of LZ-Y52 zeolite.

We prepared another batch of Ru_4ZL because we exhausted the previously prepared supply. We modified the catalyst loading method by adding the solution of $(\text{C}_2\text{H}_5)_3\text{Al}$ -treated $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ slowly to a slurry of Y-zeolite and solvent (THF). The slurry was stirred overnight to ensure an even loading on the support. We also used MgO to support the Ru_4 cluster using the same method. Both zeolite and MgO were dried under vacuum at 500°C for 10 h and then stored inside a dry box before the reaction with the organometallic. The metal loading in these two catalysts is being measured.

Task 2: Testing of Methane Reforming Catalysts

The monomeric ruthenium catalysts were tested at 750°C under 150 psig. We used 0.5 g of catalyst and the flow rate was 10 mL/min (GHSV ~ 3000 h⁻¹). Methane conversions using these monoruthenium catalysts were considerably lower than with the ruthenium clusters. The alumina-supported catalyst gave the best methane conversion of 3.04%. The 5A molecular sieve and the Na-Y zeolite-supported catalysts gave 2.34% and 1.66%, respectively. Reactions were continued for at least 15 h. During the first 2 h of the reactions, we detected small amounts of CO, which was the CO released from the ruthenium complexes. Hydrogen was the major product. Selectivity of C₂ hydrocarbons (ethane and ethylene) ranged from 1.2% to 2.8%. No higher hydrocarbons (C₃₊) were produced. Results are summarized in Table 1.

Table 1

CATALYTIC REACTION OF METHANE REFORMING

Catalyst ^a	Ru (wt%)	Flow Rate (mL/min)	Methane Conver. (%)	Selectivity ^b to		
				H ₂ (%)	C ₂ (%)	C ₆₊ (%)
Ru-com	0.50	50	71.2	151.0	-- ^c	--
Ru ₄ AL	0.61	100	10.1	78.6	1.62	--
Ru ₄ MS	0.49	100	4.9	146.6	3.52	--
Ru ₄ ZL	0.61	50	1.7	25.3	6.9	28.9
Ru ₆ AL	1.26	50	6.1	113.4	6.9	41.4
Ru ₆ MS	0.19	50	5.6	192.8	1.0	14.8
Ru ₆ ZL	0.20	50	3.6	161.9	3.6	10.0
RuAL ^d	0.35	10	3.0	139.9	2.8	--
RuMS	0.31	10	2.3	147.5	1.2	--
RuZL	0.37	10	1.7	177.5	2.6	--

^aAbbreviation: Ru-com = commercial ruthenium catalyst from Engelhard; Ru₄ = (C₂H₅)₂AlRu₄H₃(CO)₁₂; Ru₆ = (C₂H₅)₂AlRu₆H(CO)₁₈; Ru = Ru(Allyl)(CO)₂.

^bSelectivity to hydrocarbons is based on carbon number.

^cNot detected.

^dThis work.

The results show that more than one equivalent of hydrogen was produced per methane input, which suggests that some of the methane turned to coke. Previous results on the elemental analysis of the ruthenium cluster catalysts indicated that more coke was formed on alumina than the other two supports. By comparison, catalysts supported on 5A molecular sieve produce less hydrocarbon. These facts suggest that the Y-zeolite is a better choice for supporting ruthenium catalysts. However, the methane conversions on zeolite catalysts are generally lower than the other two supports.

The effect of cluster size is significant. The zeolite-supported tetraruthenium cluster (Ru_4) gave higher hydrocarbon yield than the monomer or hexamer on the same support. This result suggests that we should examine the diruthenium or triruthenium clusters and compare their yields with those of the tetramer. Methane conversion may be improved by increasing the metal loading and by the using the palladium membrane to control the hydrogen partial pressure.

We began the Phase 2 work of incorporating a Pd/Ag membrane in the reactor for hydrogen control. The reactor is designed so that the partial pressure of hydrogen inside the reactor can be controlled. A 1/16-in. Pd/Ag membrane tube is inserted inside a 1/4-in. stainless steel tube reactor, and the catalyst is loaded around the Pd/Ag tube. Helium is fed through the Pd/Ag tube while methane is fed through the catalyst bed (Figure 2). Hydrogen formed from the methane reforming reaction diffuses into the Pd/Ag tube because of a partial pressure differential. Both ends of the Pd/Ag tubing are attached to 1/8-in. stainless steel tubes by Swagelok connectors. One end is connected to helium inlet and the other end is connected to a bubbler to the GC.

We tested this reactor first using Ru_4AL because this catalyst showed the highest methane conversion of all the Ru catalysts we have synthesized. The reaction was run at 750°C and 150 psig. We used 0.5 g of catalyst and the flow rate was 20 mL/min. Hydrogen was successfully removed as observed from the GC analyses. Unfortunately, a leak developed after 10-h of reaction. The results obtained from the 10 h

FIGURE 2. REACTOR EQUIPPED WITH Pd/Ag MEMBRANE.

reaction show that the methane conversion and the hydrocarbon yield were slightly decreased compare with previous results obtained at a flow rate of 100 mL/min. We operated at a low flow rate in this experiment to maximize the hydrogen transport across the membrane.

We suspect the leak was a result of the Swagelock connection between the Pd/Ag membrane tube and the stainless steel tube which was placed inside the furnace. We modified the reactor by sealing one end of the Pd/Ag tube and placed the sealed end inside the reactor. The open end was connected to a stainless steel tube by Swagelock outside the heating area. A three-way joint was attached so that we could switch to a vacuum pump or to helium flow for controlling the partial pressure of hydrogen (Figure 3).

This new reactor was successfully used for a continuous run for ~ 72 h. However, the Pd/Ag membrane is fragile and it cracked when the reactor was emptied. Nevertheless, we tested methane reforming using Ru₄ZL under the same reaction conditions with and without hydrogen removal. The reaction was run at 750°C and 150 psig, and the flow rate was 50 mL/min. We used 500 mg of Ru₄ZL. The results show that neither

FIGURE 3. REACTOR EQUIPPED WITH Pd/Ag MEMBRANE TUBE.

the methane conversion nor the selectivity to hydrocarbon formation increases. This result suggests that the reaction was driven by kinetic force rather than the equilibrium factor.

Earlier in this project we investigated the effect of reaction conditions on the methane reforming reaction. Methane conversion increases at higher temperature and pressure. We briefly examined the effect of flow rate on Ru_6ZL . During this period, we continued this investigation by testing the same catalyst (Ru_6ZL) at four flow rates under 150 psig at 750°C . The results are shown in Table 2. Clearly, the methane conversion increases as the flow rate decreases from 500 to 50 mL/min. Further decrease in the flow rate to 5 mL/min resulted in lower conversion. The hydrocarbon yield as expressed by the C2 selectivity increases at high flow rate. The ethylene-to-ethane ratio also increases. The hydrogen yield decreases at high flow rate, which is consistent with methane conversion.

Table 2

EFFECTS OF FLOW-RATE AND PALLADIUM MEMBRANE TO THE
CATALYTIC REACTIVITY OF REFORMING CATALYSTS AT 750°C

Catalyst ^a	Flow rate (mL/min)	Methane Conver. (%)	Selectivity ^b		Ethylene/ Ethane
			H ₂ (%)	C ₂ (%)	
Ru ₄ AL	100	10.1	78.6	1.6	-- ^c
Ru ₄ AL/Pd	20	9.0	11.1	0.3	--
Ru ₆ ZL	5	11.8	49.0	1.4	0.4
Ru ₆ ZL	50	13.2	65.4	1.2	0.6
Ru ₆ ZL	300	8.1	19.7	3.7	1.48
Ru ₆ ZL	500	5.6	19.7	7.1	1.89

^aThe reaction using the Pd/Ag membrane was used in the reaction with Ru₄AL/Pd.

^bSelectivity to hydrocarbons are based on carbon number.

^cNot detected.

In the previous reporting period, we found that methane conversion on Ru₆ZL was higher at lower methane flow rates. The test was conducted using a fixed amount of catalyst (0.5 g) and the flow rate was controlled by a mass flow controller. This quarter we performed a similar test using Ru₄ZL and using 5 g of catalyst in the same reactor under the same flow rate (50 mL/min). Thus, the catalyst bed was ten times larger, which means that the residence time of the methane and the reaction products was longer. The results show that the methane conversion was markedly increased to 43%. However, the product selectivities decreased. This result suggested that the hydrocarbon products, especially the C2 hydrocarbons, were reacting further to form either wax or coke.

The hydrocarbon selectivity achieved in the test using Ru₄MgO is encouraging. The reaction was run under the same general conditions (0.5 g of catalyst, 750°C, 150 psig, and 50 mL/min) as the previous

reactions. The total hydrocarbon selectivity was 56.13% and the methane conversion was 4.04% (Table 3).

Table 3

EFFECTS OF HYDROGEN PARTIAL PRESSURE AND SUPPORTS TO THE CATALYTIC REACTIVITY OF REFORMING CATALYSTS AT 750°C

Catalyst ^a	Methane Conver(%)	Selectivity ^b		
		H ₂ (%)	C ₂ (%)	C6+
Ru ₄ ZL	6.07	99.0	0.89	2.5
Ru ₄ ZL/Pd-Vacuum	5.27	8.5	0.76	4.3
Ru ₄ ZL/Pd-He flow	5.34	77.9	0.79	2.9
Ru ₄ ZL-5 g	43.11	98.7	0.28	0.7
Ru ₄ MgO	4.04	42.82	6.88	49.2

^aRu₄AL/Pd is the reaction using the Pd/Ag membrane.

^bSelectivity to hydrocarbons are based on carbon number.

We attempted to analyze the C₆₊ components with our GC but failed. We are trying to modify our system to identify these components by changing to other GC columns and sampling methods. Since our results show that lower space velocity increases the methane conversion, we will build a larger reactor that can hold more catalyst but form a thinner bed. We are going to test the mixed metal catalyst and synthesize other mixed metal clusters. Using MgO as the support seems promising and we will continue investigation of this system.

Task 3: Synthesis of Oxidation Catalysts for Methane

We began synthesizing zeolite-encapsulated tetramesitylporphyrin (TMP). Zeolite powder, zinc acetate, mesitylaldehyde, pyrrol, and pyridine are sealed in a glass reactor under oxygen atmosphere and heated at 180°C for 48 h. After the mixture is washed with large

amounts of acetone, the purple zeolite still contains ZnTMP which can be removed with chloroform.

The zeolite encapsulated zinc tetra-mesitylporphyrin (TMP) synthesized last quarter was demetallated using HCl. The dichloromethane solution of ZnZLTMP was stirred with 1 N aqueous HCl for 2 h and then washed with water. Ruthenium was inserted by refluxing the DMF solution of $\text{Ru}_3\text{CO}_{12}$ and TMPH_2 -zeolite for 1 h. The product was washed with water and methanol.

FUTURE WORK

The goals of this research project are to increase the methane conversion and improve the hydrocarbon production. For methane reforming, we achieved a conversion of up to 43% by adjusting the reaction conditions. Ruthenium clusters are effective catalysts but the selectivity to hydrocarbons needs to be improved. In evaluating the effect of cluster size for mononuclear, tetranuclear, and hexanuclear ruthenium complexes we found that the tetraruthenium cluster was by far the most effective catalyst. We began to study the mixed metal catalysts by synthesizing a FeRu_3 cluster. We plan to vary the ratio of Fe to Ru by synthesizing Fe_2Ru_2 and Fe_3Ru clusters.

The type of the support also plays an important role in methane reforming. We briefly tested a basic support, magnesia, in addition to the acidic supports tested previously (alumina, 5A molecular sieve, and Y-zeolite). The results are promising. We will continue to investigate the role of the support.

The effectiveness of using a hydrogen removal membrane is still in question. We purchased a new Pd/Ag membrane tube inside which a stainless steel spring is inserted. The steel spring will increase the strength of the otherwise fragile tube and it will support the tube during bending. We will build a new reactor using this membrane tube.

During the next quarter, we will focus more on methane oxidation. The stability of the catalysts is one of our concerns. In addition to synthesizing novel catalysts, we will also investigate the effect of adding an axial base such as N-methyl imidazole.

EXPERIMENTAL DETAILS

Preparation of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$

A THF (120 mL) solution containing $\text{Ru}_3(\text{CO})_{12}$ (300 mg, Aldrich) was added dropwise over a 30 min to a refluxing THF (250 mL) solution of $\text{Na}_2[\text{Fe}(\text{CO})_4]$ (210 mg, Aldrich). The solution was then refluxed for 1 h. The solvent was immediately removed from the deep-red solution under vacuum. Deoxygenated hexane (120 mL) was added to the brown residue and followed by the addition of deoxygenated H_3PO_4 (40 mL). The hexane layer was separated, dried over anhydrous MgSO_4 for 1 h, and then filtered. The brown solution was concentrated to 60 mL and chromatographed on silica gel. Hexane was used as eluent to remove $\text{Ru}_3(\text{CO})_{12}$, $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, and $\text{Fe}_3(\text{CO})_{12}$. A solution of 10% acetone in hexane was used to elute the red $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$. The product was recrystallized in hexane (yield 40 mg, 11.7%).

Preparation of Zeolite Encapsulated Tetramesitylporphyrins (TMPH₂)

Zn-Y zeolite (10 g), was prepared by the metal ion exchange method using ZnCl_2 (metal weight loading was about 2%). This zeolite was moved with mesitylaldehyde (3.6 g), pyrrole (1.6 g), and pyridine (0.5 mL) and was added into a quartz tube that was placed inside a Parr bomb. The mixture was flushed with oxygen and sealed. The Parr bomb was heated at 180°C for 2 days. The brown zeolite was removed and washed with a large amount of acetone.

The resulting zeolite was stirred in 6 N HCl for 2 h to remove zinc and then washed with water and 2 N NH_4OH . The zeolite was then washed again with water and dried at 150°C under vacuum for 2 days.

Ruthenium Insertion into TMP-Zeolite

To insert ruthenium into TMP-zeolite, we used a procedure similar to that used to insert metal into the TPP-zeolite as reported in the

last quarterly report. In a three-necked round bottom flask, TMP-zeolite (5 g) and $\text{Ru}_3(\text{CO})_{12}$ (0.5 g) and 100 mL of dimethyl formamide (dried over 4A molecular sieve) were added. The mixture was heated to reflux for 1 h. The product was washed with water, methanol, and dried in vacuum oven at 150°C for 2 days.

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