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DIRECT CATALYTIC CONVERSION OF METHANE AND LIGHT HYDROCARBON GASES

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I 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. SRI project 2678 (sponsored by the U.S. Department of Energy's Pittsburgh Energy Technology Center--DOE-PETC--under contract DE-AC22-86PC90011) is exploring two approaches to achieving the stated goal.

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.

We will test the catalysts in a fixed-bed isothermal microreactor in a downflow mode at ~100 psi. SRI will use an automated two-column gas chromatograph (GC) to analyze the reactor effluent for products and conversion of reactants. Commercial reforming catalysts and oxidation catalysts will be used to establish performance baselines for the reforming and oxidation of methane, respectively. We will characterize the catalysts before and after each run to establish the chemical nature of the catalyst, its oxidation state, and dispersion.

During the first quarter of this project, we have concentrated on methane oxidation to methanol. We have synthesized phthalocyanine oxidation catalysts containing different metals (Co, Fe, and Ru) within zeolite pores. Our examination of their ability to oxidize methane to methanol has indicated preliminary positive results.

II 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 will 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 will 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 (e.g., 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) on the techniques of surface-confinement to produce novel catalysts for a wide variety of processes.[5,6,7-25] The stability of surface-confined carbonyl clusters has been questioned.[26] 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)].

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

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 Rh complexes, Rh_2(2-hydroxy-6-methylpyridine). Clusters will be prepared from the hydridocarbonyl clusters by relying on reactions like (2) and (3).

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

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

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, which 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 flowrate.

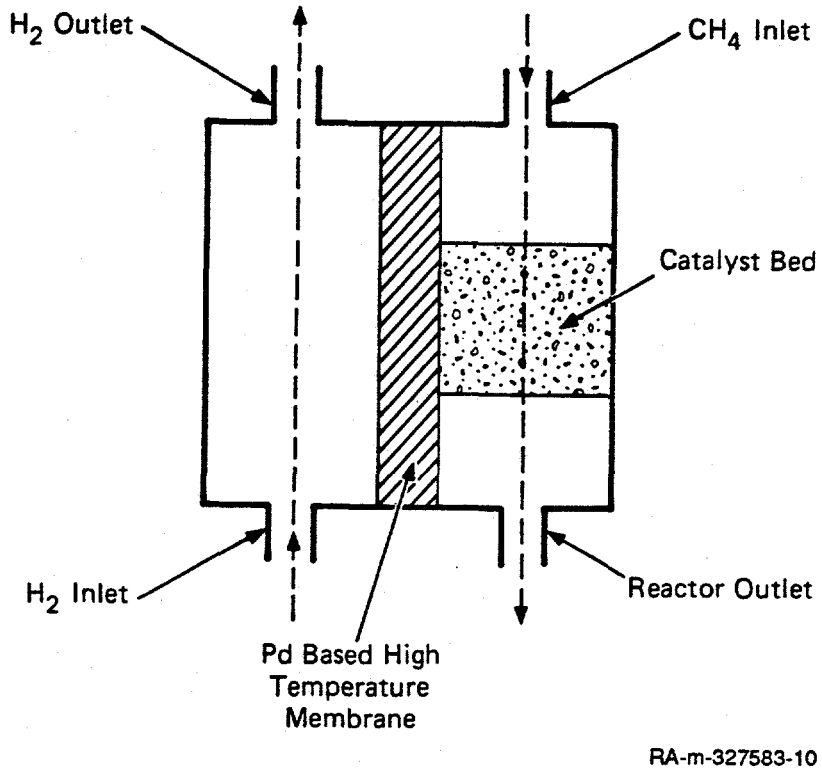


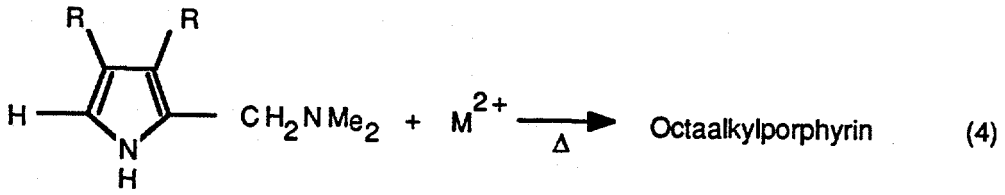
FIGURE 1 SCHEMATIC OF REACTOR WITH MEMBRANE FOR HYDROGEN CONTROL

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 (14)] will give the desired porphyrin.



(4)

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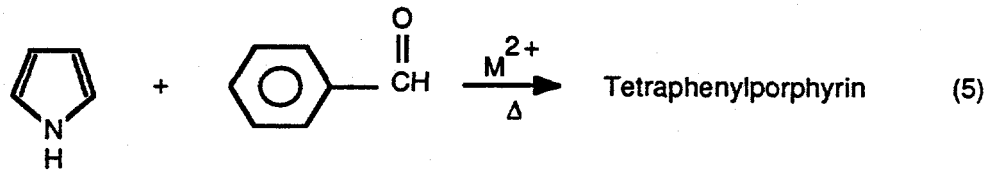
Alternatively, the cocondensation of pyrrole with benzaldehyde will give tetraphenylporphyrin [equation (5)].[30]



(5)

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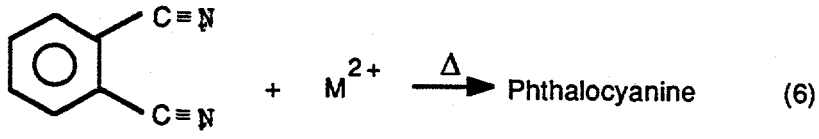
The phthalocyanines are produced by the condensation of phthalonitriles [equation (6)].



(6)

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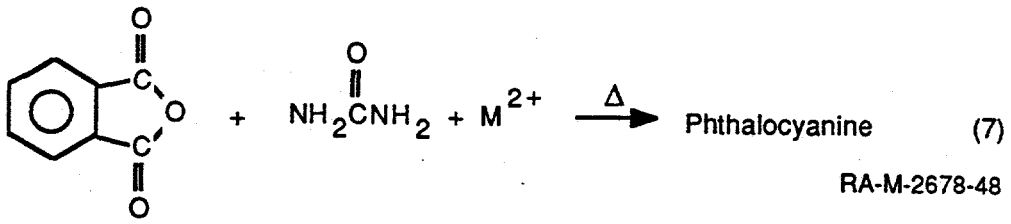
Alternatively the condensation of phthalic anhydride and urea produces phthalocyanine [equation (7)][31]



Task 4: Testing of Methane Oxidation Catalysts

SRI will test methane oxidation catalysts in the same fixed-bed isothermal downflow 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 thus 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 quite strong. IR will be measured and compared with literature studies of surface-confined clusters.[35-39] In addition, Ozin has 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 around 20 Å and will be used to confirm other measurements.

RESULTS AND DISCUSSION

During the past 3 months, we have synthesized reforming catalysts and oxidation catalysts (Task 1 and 3), worked on assembling the automated microreactor, and tested the oxidation catalysts in a nonquantitative reactor mode. We will limit our discussion here to the oxidation catalysts (Tasks 3 and Task 4) because the methane reforming catalysts are better tested on an automated system in which the product gas mixture is directly sampled by the GC. However, because for methane oxidation the product (e.g., methanol) is condensable a relatively simple system will allow us to qualitatively test the oxidation catalysts.

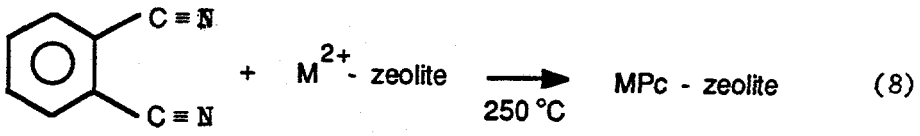
We have received and installed the Carle CGC-500 gas chromatograph (GC), which will allow the analysis a wide range of gas samples--from hydrogen to C_{12} hydrocarbons on a single injection. We are automating the reaction system to connect the Carle GC with it. This system will include flow controllers and high-pressure fittings that will provide a wide range of flexibility in varying the reaction conditions. Once the system is fully integrated, we will be able to quantitively measure conversions and yields for both types of reactions.

We have synthesized several zeolite encapsulated phthalocyanine complexes and have tested their reactivity for oxidation of methane. The results are described in the following sections.

Task 3: Synthesis of Oxidation Catalysts for Methane

The strategy for synthesizing oxidation catalysts in this task is to encapsulate porphyrin or phthalocyanine metal complexes in zeolites. To do so, we first exchange the sodium ion in the γ-zeolite with the desired metal ion. The porphyrin or phthalocyanine complexes will then be synthesized by template condensation. We have prepared zeolite encapsulated phthalocyanine complexes of Co, Fe, and Ru by this

method shown in equation (8).



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The formation of the phthalocyanine complexes is easily confirmed by their distinctive blue-green color. Treatment of the supported catalyst with concentrated sulfuric acid dissolves some of the metal complex. The visible-UV spectra of the sulfuric acid solutions are identical to those of the commercial phthalocyanine complexes (see Figure 2). If metallophthalocyanine can be removed from the zeolite that may indicate that some of it was formed on the zeolite surface (i.e., outside of the pores) and reamined even after washing with methanol and heat treatment (150°C) under vacuum. If that is the case, our preparation method should be modified to include a sulfuric acid extraction and perhaps an ion exchange step. Elemental analyses show that the zeolite catalysts contain 1% to 2% metals (see Table 1). As expected, the metal content remains the same after phthalocyanine synthesis. However, the carbon content indicative of the organic portion is usually higher than the theoretical value. This suggests that some of the phthalocyanine precursor (phthalonitrile) or its decomposition product is adsorbed by the zeolite. Heating the catalysts at higher temperature (~ 500°C) or the sulfuric acid extraction should remove the excess ligand.

To study the effect of axial ligand on the reactivity of these catalysts, we treated them with excess pyridine, which should give the dipyridine adducts of the metallophthalocyanines. Samples of these catalysts have been sent for elemental analysis.

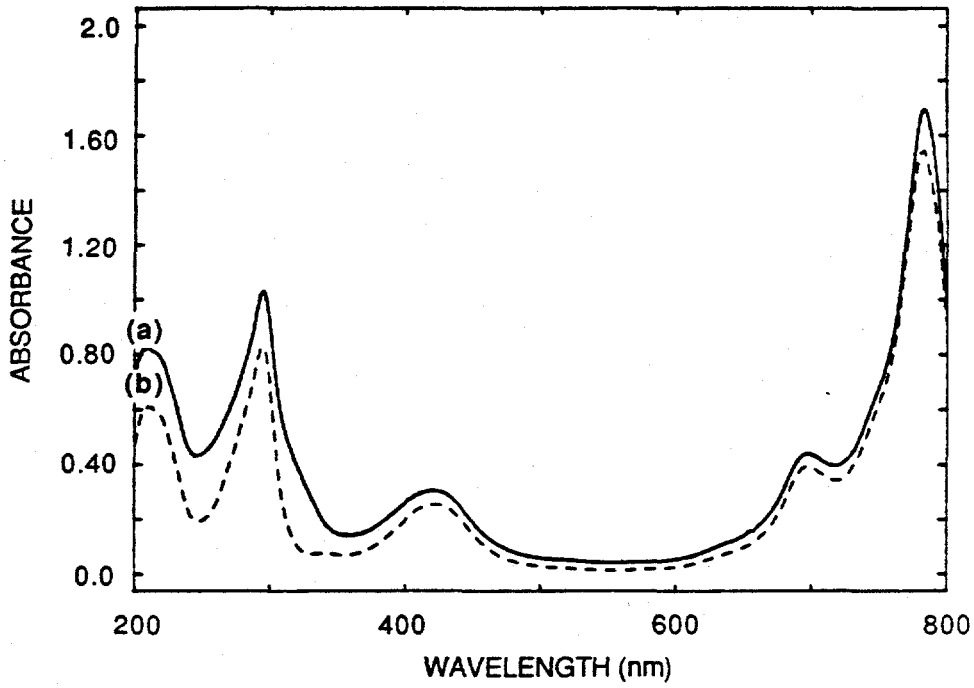


FIGURE 2 VISIBLE-UV SPECTRA OF COBALT PHTHALOCYANE IN CONCENTRATED SULFERIC ACID

(a) Zeolite encapsulated CoPc synthesized in this project
(b) Commercial CoPc

Table 1

ELEMENTAL ANALYSES OF ZEOLITE CONFINED PHTHALOCYANINE COMPLEXES

Catalyst	Conditions	Element Content (% wt) Carbon	Hydrogen	Metal
CoPc	Before reaction	14.53	1.59	1.96
	After reaction	14.49	1.99	2.00
FePc	Before reaction	25.61	1.80	1.19
	After reaction	11.68	0.70	1.60
RuPc	Before reaction	17.35	1.87	1.58
	After reaction	18.15	1.95	1.74

Task 4: Testing of Methane Oxidation Catalysts

We have set up a relatively simple isothermal downflow reactor system to test the oxidation catalysts prepared in Task 3. The system is described in Section II. The catalysts were tested in a glass reactor. All three catalysts (without pyridine treatment) were tested at 200°C under atmospheric pressure. Neither GC nor ^{1}H NMR spectroscopy detected methanol during a 24 h run. The liquids collected from each run contain water and small amounts of aromatic compounds. We do not know whether the aromatic compounds result from decomposition of phthalocyanine or from unreacted organic starting materials that were trapped inside the zeolite pore. The elemental analyses of these catalysts always show a higher carbon content than is required for phthalocyanine complexes with respect to the metal content. As observed from the elemental analyses, little change in the carbon, hydrogen, and metal content occurs on reaction except in the case of iron phthalocyanine (see Table 1). This indicates that the metallophthalocyanines are stable under the reaction conditions. In the case of the FePc catalyst, more than 50% of carbon and hydrogen were lost, and the percentage of iron increased. Although all three catalysts were treated by the same procedure, a larger amount of organic compounds may have been trapped in the zeolite pore of the FePc catalyst than in the other two cases. This is indicated by an unusually high carbon content in the fresh FePc catalyst.

Because glass beads catalyze the oxidation of methane to methanol, we switched to a stainless steel reactor and reexamined the RuPc catalyst. Under the same reaction conditions (flow rate, temperature, pressure, and reaction time), small amounts of methanol, together with water and some unidentified product, were formed. Surprisingly, no aromatic compound was detected. A ^{1}H NMR spectrum is shown in Figure 3. The peak at 3.46 ppm is due to the methyl protons on the methanol. Large amounts of water are formed as shown by the board peak at 4.80 ppm. The compounds responsible for the sharp peak 2.147 and a board peak at 1.747 have not yet been identified. An amine compound, which does not come from methane oxidation may be responsible. Further investigation is under way.

The formation of methanol was confirmed by GC/MS. No methanol was formed in the absence of RuPc. We ran blanks over the zeolite and the Ru exchanged zeolite and observed no methanol formation. This result is encouraging, and we will reexamine the other metallophthalocyanine complexes in the stainless steel reactor.

Future Work

We have observed the successful conversion of methane to methanol in the presence of the Ru phthalocyanine zeolite confined catalyst. Other variables including space velocity, methane-to-oxygen ratio, temperature, and pressure. We should also examine the cooling rate needed to discourage the secondary oxidation process, which produces unwanted carbon oxides.

We are setting up a more sophisticated reactor system that will include an online GC monitoring unit. This system will allow us not only to control the variables more precisely, but to analyze both the condensable gas and light gases such as methane and the carbon oxides.

Future work on the synthesis of oxidation catalysts will include evaluations of the variations in the metal and the peripheral substituents of other phthalocyanine complexes. Although the catalytic reactivity is mainly governed by the central metal ion, the peripheral

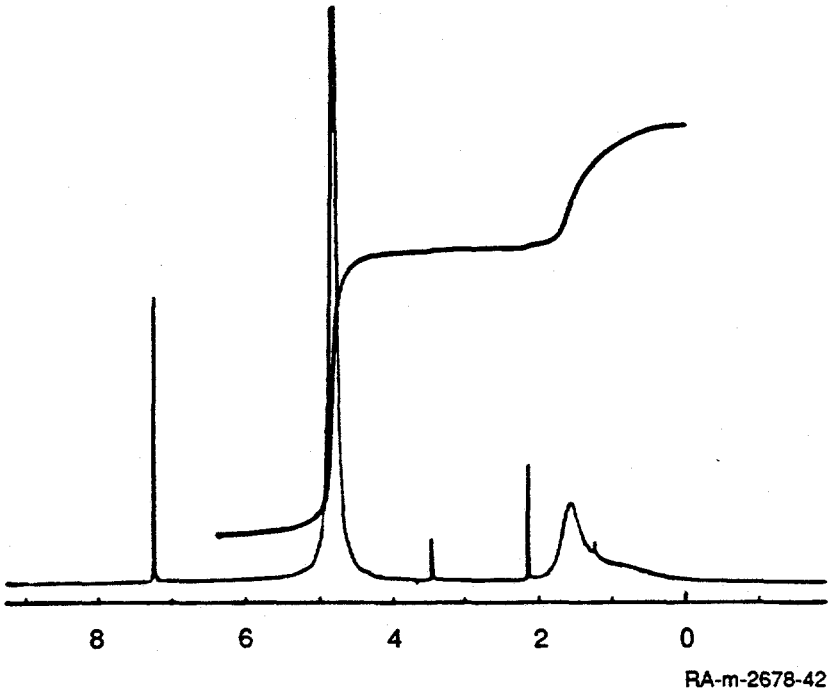


FIGURE 3 PROTON NMR SPECTRUM OF THE LOQUIDE PRODUCT OBTAINED FOR THE RuPc-ZEOLITE CATALYZED METHANE OXIDATION

substituents will also have a minor influence on the electronic structure of the metal and therefore on reactivity. The different derivatives of phthalocyanine (e.g., tetrasulfophthalocyanine) will decrease the mobility of the metal complex because of their larger moleculars and their ionic attraction.

For the methane reforming process, we will continue to work on the organometallic anchored zeolite catalysts. In addition to Ru clusters, we will also synthesize mixed metal clusters with variations in the metals and the cluster size. In preparing these catalysts the anchoring process will be a key step. We will develop a method for characterizing the catalysts.

Experimental Details

Preparation of Metal Ion Exchanged Zeolite

y-Zeolite (50 g) (LZ-Y52, Union Carbide) containing 10.4% sodium oxide is stirred in a 0.2 M aqueous solution (20 mL) of metal salt ($CoCl_2 \cdot 4H_2O$ or $FeCl_2 \cdot 4H_2O$) for 24 h. The solution is discarded, and the zeolite is washed at least 3 times with water until the liquid is clear. The zeolite is then dried at 110°C under vacuum for 24 h. Ru zeolite is prepared by a similar procedure, except that a methanol solution of Ru dodecarbonyl is used and that methanol is used to wash the zeolite.

Synthesis of Metallophthalocyanine

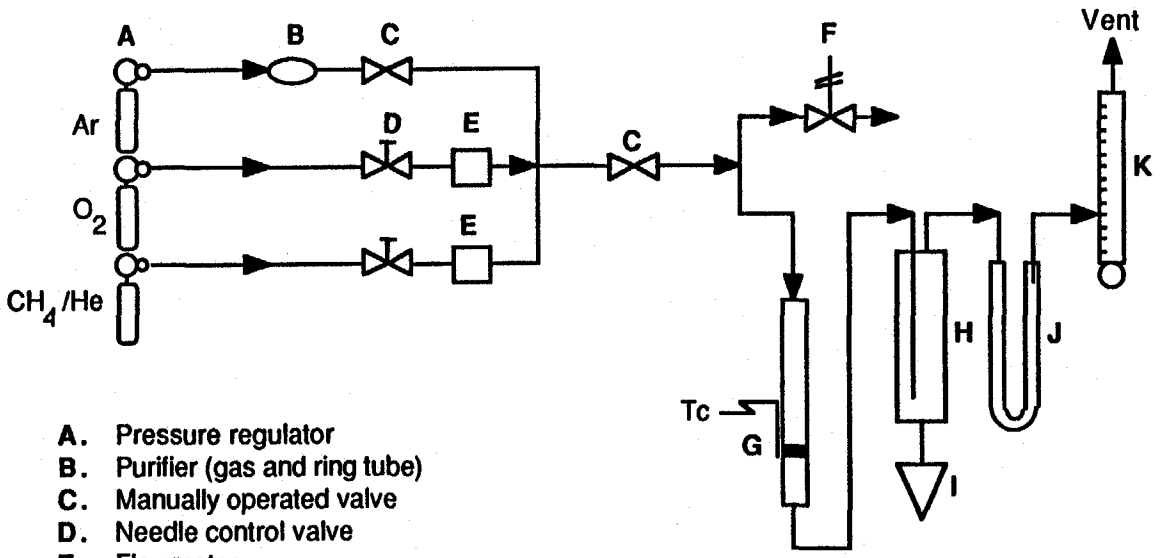
A mixture of 10 g of dicyanobenzene (Aldrich) and 20 g of transition metal containing zeolite is ground to powder and added to a 100-mL round bottom flask equipped with a reflux condenser. The mixture is heated to 250°C for 6 h. The formation of phthalocyanine is indicated when by the color changes to green. The green powder is allowed to cool to ambient temperature and is then washed 3 times with excess methanol until the liquid is clear. The resulting product is then sublimed at 150°C under vacuum (~ 1 mmHg) for 2 h.

Physical Measurements

Vis-UV spectra are measured with a Hewlett-Packard 8650A spectrophotometer. Proton NMR spectra are recorded on a JEOL FX-90Q variable probe spectrometer. Samples of the liquid product obtained from the methane reactions are added to a 5-mm tube containing 99.8% deuterate chloroform.

Testing of Methane Oxidation Catalysts

We have set up a relatively simple isothermal down flow reactor to test the oxidation catalysts (see Figure 4). The catalyst is first heated under argon flow at 200°C to remove vaporizable impurities such as water. The methane used is diluted with 90% helium, primarily for safety reason. The methane and oxygen flow rates are controlled by needle valves and the exhausted gas is passed through a cold trap (dry ice/ethanol) at - 78°C and then through an oil filled bubbler. A soap-film flow meter connected to the end of the bubbler checks the flow rate periodically. The liquid collected in the cold trap is allowed to warm to room temperature at the end of the reaction. The methane-to-oxygen ratio was set at 2:1; the total flow rate is 100 mL/min. We use 1 g of catalyst for each run, and each run was followed for 24 h.



A. Pressure regulator
B. Purifier (gas and ring tube)
C. Manually operated valve
D. Needle control valve
E. Flowmeter
F. Pressure relief valve, cracks at indicated pressure (50 psi)
G. Reactor
H. Condenser
I. Liquid collector
J. Babbler
K. Soap-film slow meter

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FIGURE 4 ISOTHERMAL REACTION LIMIT

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