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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 gasification of 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 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 later can be converted to either liquid fuels or value-added chemicals, as economics dictate.

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 have synthesized and tested several novel catalysts for methane reforming (Tasks 1 and 2) and for partial oxidation of methane (Tasks 3 and 4). We started to test a mixed metal system, an $FeRu_3$ cluster. This catalyst was supported both on zeolite and on magnesium oxide and the systems were tested for methane reforming at various reaction temperatures. We also prepared and tested a monomeric ruthenium catalyst supported on magnesium oxide. We found that methane is activated at a lower temperature with the basic magnesium oxide support than with acidic supports such as zeolite or alumina. Methane conversions increased with temperature, but the production of coke also increased.

We prepared a sterically hindered ruthenium porphyrin encapsulated in a zeolite supercage for catalysis of methane oxidation. The results showed that only carbon dioxide was produced. Addition of axial base to this catalyst gave similar results. Another type of catalyst, cobalt Schiff base complexes, was also prepared and tested for methane oxidation. In this case, no methane conversion was observed at temperatures ranging from 200° to 450°C. These complexes do not appear to be stable under the reaction conditions.

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 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, with an emphasis on Re and Ru clusters of 2-4 metal atoms are used as catalyst precursors.

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

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[*] 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.

questioned,[26] we are attempting to prepare catalysts whose surface binding is better characterized. Therefore, we are studying catalysts of the Yermakov type, which are anchored by direct reaction with the surface [equation (1)].

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

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 began with the following compounds: For Re, we are using $Re_2(CH_2SiMe_3)$ and $Re_3(CH_3)_9(Py)_3$; 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).

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

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

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 gas chromatograph (GC) is used to monitor 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 <u>insitu</u> 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.

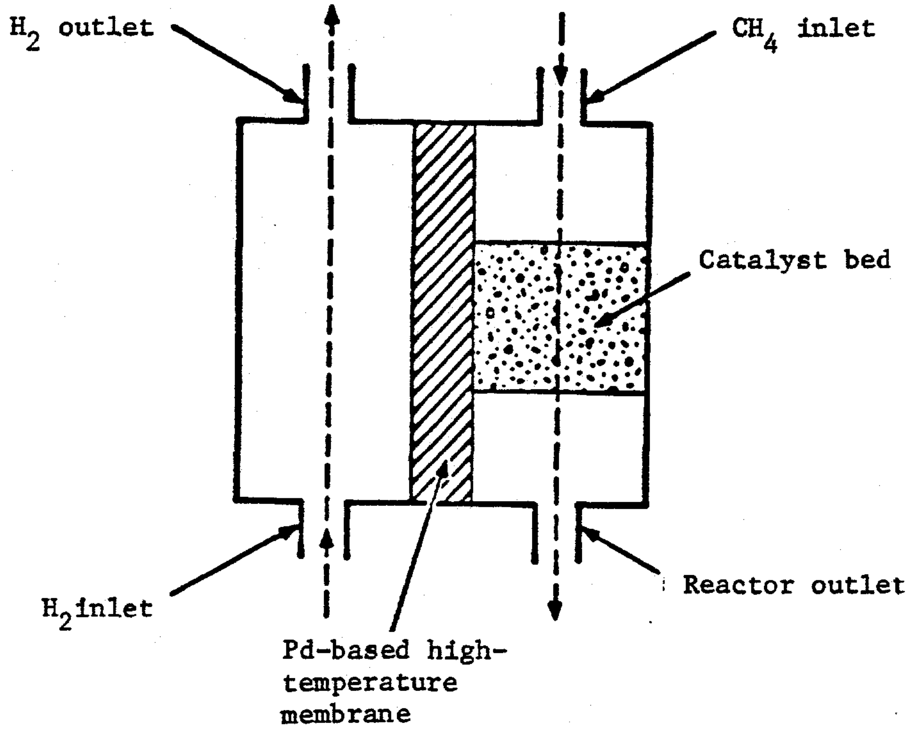

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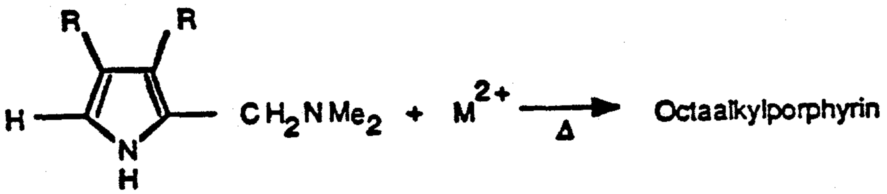
FIGURE 1. SCHEMATIC OF REACTOR WITH MEMBRANE FOR HYDROGEN CONTROL.

<u>Task 3: Synthesis of Oxidation Catalysts for Methane</u>

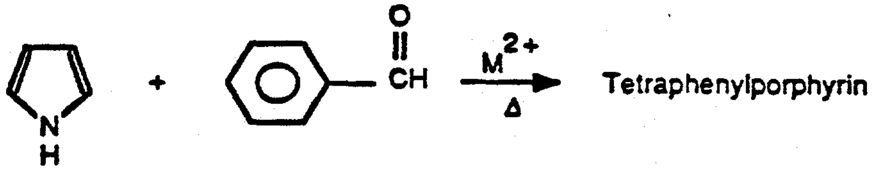
In Task 3, we are synthesizing oxidation catalysts by encapsulating porphyrin and phthalocyanine metal complexes in zeolites. Variables include the porphyrin or phthalocyanine ligand, the type of metal, and the type of zeolite. The metal complexes used are Cr, Mn, Re, Ru, and/or Co, with emphasis on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

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.



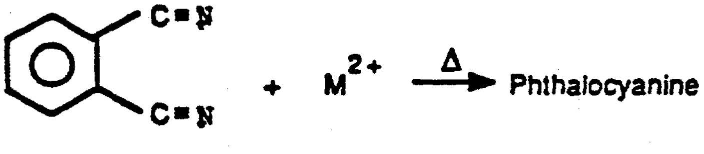
(4)

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



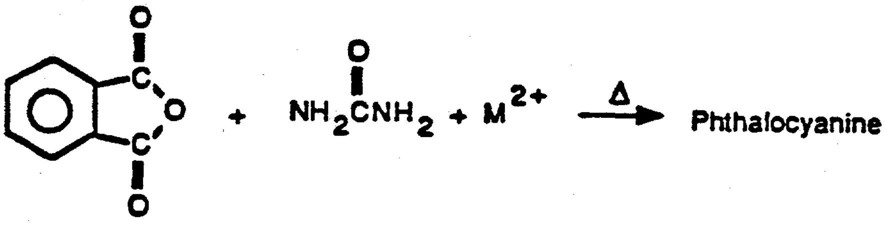
(5)

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



(6)

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



(7)

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, using an automated two-column GC to monitor 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

In the last reporting period, we observed that a magnesia supported mixed iron and ruthenium tetrameric complex catalyzed methane reforming at lower temperatures than did the pure Ru clusters. During this period, we investigated whether the low temperature reactivity was due to the support or to the metal complex. A magnesia supported Ru monomer and a zeolite supported $FeRu_3$ cluster were tested at various temperatures. The results show that methane conversion was higher on the magnesia supported catalysts but the hydrocarbon selectivity was controlled by the metallic components of these catalysts. The mixed metal catalyst, $FeRu_3$, gave a higher hydrocarbon yield than the ruthenium catalysts. The selectivity to hydrocarbons decreased with increasing temperature.

The results from tests using the magnesium oxide supported catalysts are quite different from those using catalysts with acidic supports (alumina, molecular sieve, and Y-zeolite): the MgO supported $FeRu_3$ cluster is active at a lower temperature (450°C). The C_2 hydrocarbon yield decreases with temperature, but the methane conversion and the hydrogen yield increase with temperature. However, no hydrocarbon above C_2 was detected in tests of MgO supported catalysts, in contrast to the results of tests of catalysts with acidic supports.

When we tested the zeolite encapsulated RuTMP on methane oxidation, only carbon dioxide was detected in the product gas. Addition of an axial base, N-methyl imidazole, to RuTMPZL and RuTPPZL did not increase the selectivity.

We prepared another type of zeolite-encapsulated oxidation catalyst: cobalt Schiff base complexes. It is known that cobalt Schiff bases catalyze the oxidation of methyl indole[32] and the zeolite-encapsulated Schiff base complexes have been used for oxygen carriers.[33] Two zeolite-encapsulated Schiff bases were prepared and tested for methane oxidation, but our results showed that neither catalyst was active for the catalysis of methane oxidation. The complexes may have decomposed early in the reaction.

Task 1: Synthesis of Advanced Reforming Catalysts for Methane

We prepared the MgO supported monomeric Ru complex by direct reaction of Na(allyl)Ru(CO)$_3$ with the basic support. The resulting catalyst contains only 0.20% Ru (by weight). It may be coincidental that all the MgO supported catalysts prepared contain 0.2-0.25% metal. The Ru$_4$MgO contains 0.25% Ru, and the FeRu$_3$MgO contains 0.11% Ru and 0.14% Fe (total metal weight is 0.25%). Although the amount of metal complex we used should give a 1% metal loading, the resulting metal content was much lower. Excess metal complex might have been removed under vacuum, leaving the tightly bonded metal complexes. In the FeRu$_3$MgO, the ratio of Fe to Ru does not agree with the formulation, which implies that the complex may have decomposed.

Task 2: Testing of Methane Reforming Catalysts

The major difficulty of GC analysis is the sampling volume because of the variation of temperature and pressure. To obtain more accurate analysis, we used a mixed gas contained 20.1% methane, 20.2% nitrogen and 59.7% helium as the feed gas. The nitrogen is used as an internal standard. The reactor was constructed with 3/8-inch (O.D.) stainless steel, and generally 2 g of catalyst was used.

We tested three magnesia supported catalysts. The results are listed in Table 1 with those of zeolite supported analogs. At the same reaction temperature, the magnesia supported tetraruthenium cluster, gave a higher hydrocarbon yield than the zeolite supported tetraruthenium cluster. The methane conversion was lower. We used the same procedure to prepare these two catalysts, the resulting catalysts contained 0.25% ruthenium for Ru$_4$MgO and 0.14% for Ru$_4$ZL. The difference in reactivity might be affected by the difference in metal loading as well as by the type of support.

Table 1

CATALYTIC REACTIVITY OF ZEOLITE AND MAGNESIA SUPPORTED CTALYSTS FOR METHANE REFORMING[a]

Catalyst	Temp (°C)	Methane Conversion (%)	Selectivity (%)[b]	
			C_2	C_{6+}
Ru_4ZL	750	6.07	0.9	2.5
Ru_4MgO	750	4.04	6.9	49.2
RuZL	750	1.7	2.6	--[c]
RuMgO	600	21.044	0.1	0.5
$FeRu_3ZL$	600	3.07	1.9	18.5
$FeRu_3MgO$	600	8.87	0.1	--

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[a] Reaction conditions: pressure = 150 psig, flow rate = 20 ml/min, weight of catalyst = 2 g, stainless steel reactor O.D = 3/8 in.
[b] Selectivity to hydrocarbon is based on carbon number.
[c] Not detected.

Methane conversion is much higher with the magnesia supported ruthenium monomer and the $FeRu_3$ cluster than with the zeolite supported analogs. However, the product selectivities to hydrocarbons are lower. The RuZL contained 0.37% ruthenium and was tested at 750°C. The RuMgO contained only 0.2% ruthenium, but its reactivity was higher even at a lower temperature (600°C). At 750°C, the RuMgO gave a 45.7% conversion of methane, but no hydrocarbon product was detected. At 600°C, the methane conversion was 8.87% for $FeRu_3MgO$ and 3.07% for $FeRu_3ZL$. At 750°C, methane conversion increased to 41.5% for $FeRu_3MgO$ and 23.05% for $FeRu_3ZL$. These catalysts, like the ruthenium monomers, produced lower hydrocarbon yields on the magnesia supported than on the zeolite support.

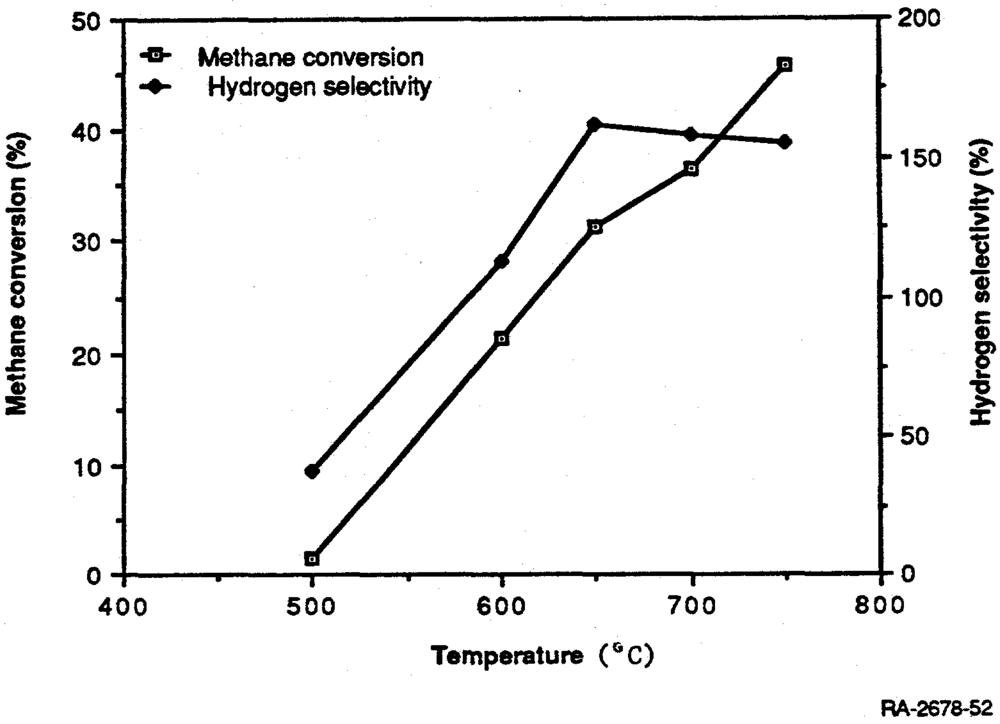

Figure 2. EFFECTS OF TEMPERATURE ON METHANE CONVERSION AND HYDROGEN SELECTIVITY OF RuMgO.

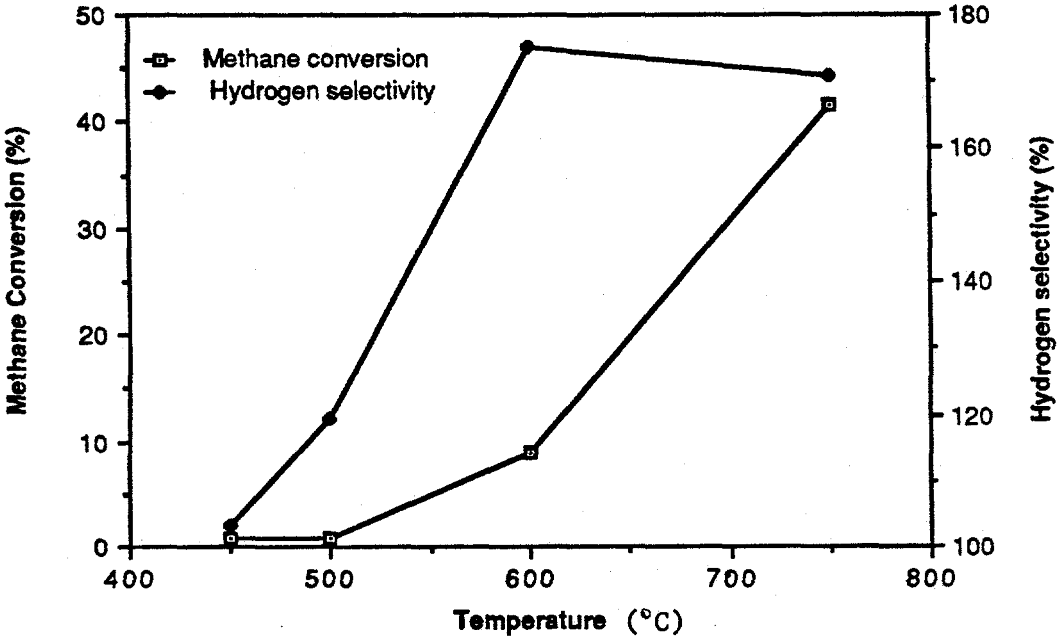

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Figure 3. EFFECTS OF TEMPERATURE ON METHANE CONVERSION AND HYDROGEN SELECTIVITY OF $FeRu_3MgO$.

Increased reaction temperature generally increases the methane conversion on the magnesia supported catalysts. Figure 2 and 3 show the effects of increasing temperature on methane conversion and hydrogen selectivity. More than 40% of methane was converted in both RuMgO and $FeRu_3MgO$ reactions at 750°C. Hydrogen selectivities were lower at lower temperatures. At high temperatures (>600°C), the hydrogen selectivities were larger than 100% of the reacted methane, which suggests coke formation. Hydrocarbon yields were low in both cases.

Increased temperature had a similar effect on the methane conversion over $FeRu_3ZL$, but methane conversion was lower with $FeRu_3ZL$ than with MgO supported catalysts. At 750°C, methane conversion with $FeRu_3ZL$ was 23.05%. Hydrocarbon yields increased as the reaction temperature increased from 500° to 600°C, then declined at higher temperatures. The maximum yield of C_2 was 0.06% of the input methane; the maximum yield of C_{6+} was 0.57%. Ru_4ZL was essentially nonactive at 600°C, so this low-temperature reactivity of $FeRu_3ZL$ is obviously due to an effect of the mixed metal: introduction of the iron to the metal cluster is advantageous to methane dehydrogenation activity. Figure 4 shows the effects of increasing temperature on methane conversion and hydrocarbon yield. The highest hydrocarbon yield was obtained at 600°C; however, the hydrogen selectivity was 170% at this temperature, which suggests coke formation.

Task 3: Synthesis of Oxidation Catalysts for Methane

The axial base of macrocyclic metal complexes usually plays an important role in the reactivity of the central metal atom. We treated the zeolite-encapsulated porphyrin complexes with N-methyl imidazole, a strong coordinating base that is known to increase the metal-oxygen binding. After being stirred in N-methyl imidazole for 2 h, the catalyst was washed with acetone and placed in an vacuum oven at 60°C overnight.

The Schiff base catalysts were synthesized by first ion-exchanging the cobalt ions in LZ-Y52 zeolite. Salicylaldehyde and diamines were

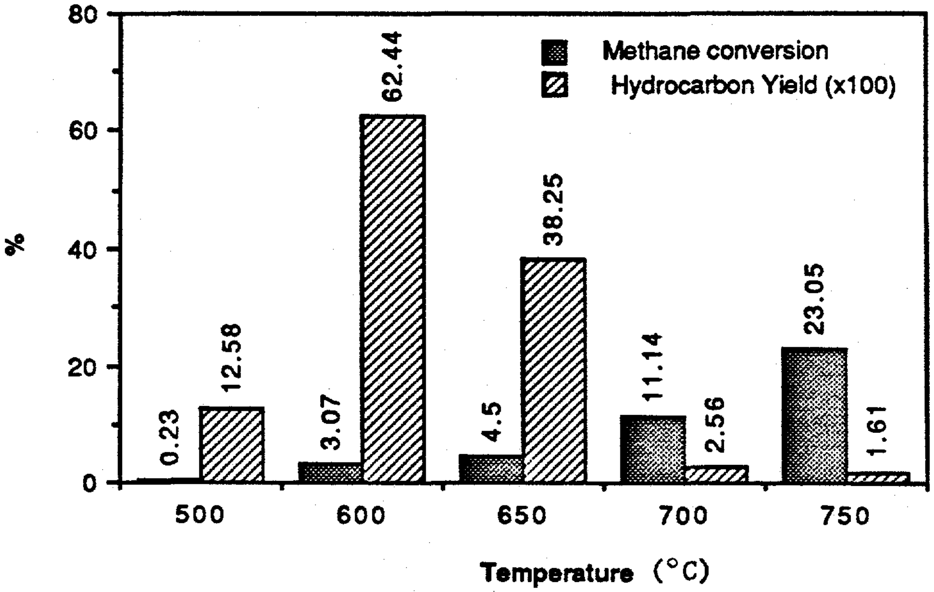

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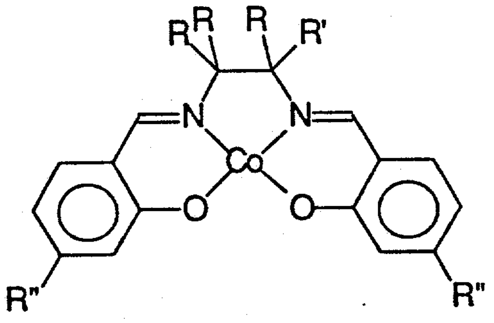
Figure 4. EFFECTS OF TEMPERATURE ON METHANE CONVERSION AND HYDROCARBON YIELD OF $FeRu_3ZL$.

dissolved in ethanol and mixed with the cobalt zeolite. The mixture was heated to reflux overnight and then filtered. The complexes were formed inside the supercages and also in the channels and on the surface of the zeolite. After the zeolite was air dried, the surface adsorbed metal complexes, and metal-free Schiff bases were extracted with methylene chloride. Excess cobalt ions were back exchanged with sodium acetate in ethanol. The axial base 1-methyl imidazole was then added to the zeolite catalysts.

We prepared two different Schiff bases: [(1,2-diaminopropylene)bis-salicylideniminato]Co(II), CoSalPn (1); and [N,N'-(1,1,2,2-tetramethyl-ethylene)bis-(4-methoxysalicylideniminato)] Co(II), CoVan4TMen (2). Their structures are shown in Scheme 1. CoVan4Tmen is sterically hindered compared to the CoSalPn. Metal loading on the CoSalPn-ZL is 0.7%; for Covan4TMen-ZL, it is 1.5%.



1.CoSalPn : R=H, $R'=CH_3$, R"= H

2. CoVan4TMen : $R=R'=CH_3$, $R'' =OCH_3$

Scheme 1. STRUCTURE OF COBALT SCHIFF BASES

Task 4: Testing of Methane Oxidation Catalysts

We tested the zeolite-encapsulated ruthenium tetramesityl-porphyrin (RuTMP) for methane oxidation at temperatures ranging from 200° to 450°C, a pressure of 50 psig and a methane/oxygen ratio of 4 we observed no reactivity for methanol production. Treatment with N-methyl imidazole did not improve the result. Carbon dioxide was the only product detected with or without base treatment. Another catalyst, RuTPPZL, lost its activity after treatment with N-methyl imidazole.

We tested the two Schiff base catalysts for methane oxidation in the temperature range from 250° to 450°C, using a methane to oxygen ratio of 5 a flow rate of 50 mL/min and a pressure of 1 atm. Nitrogen was used as an internal GC standard. Both catalysts were inactive as indicated by zero methane conversion. During the first reaction cycle, some hydrocarbons (C_2-C_{6+}) were released; the hydrocarbon release was probably due to ligand decomposition or decomposition of excess axial base. The catalysts changed from light brown to dark brown, also suggesting possible ligand decomposition.

FUTURE WORK

Our results show that the mixed metal catalyst is better than the catalysts containing only ruthenium because it catalyzes methane dehydrogenation at lower temperatures. We plan to continue to study the mixed metal system. A variety of mixed metal complexes will be synthesized and tested. The use of magnesium oxide to support the ruthenium complexes gave higher methane conversion activity than that found with acidic supports, but for the $FeRu_3$ cluster, the hydrocarbon yield was higher on the zeolite support than on the magnesia. We will study further the difference in activities of these two support materials.

Since the Schiff bases are not stable at high temperatures, we will not continue to study this type of compound. The porphyrins and phthalocyanines are much more stable than these Schiff bases. Some of the phthalocyanines and porphyrins have shown catalytic activity for methane oxidation in our previous studies and we will continue to study these two systems.

We have tried to use a Pd/Ag membrane to remove hydrogen from the reactor bed, but the reactor was not reusable because the Pd/Ag tube was so fragile. We have purchased new Pd/Ag tubing in which a spring was inserted to stabilize the tubing and are building another reactor using this new Pd/Ag tubing to study the effect of hydrogen partial pressure on some of the catalysts.

We must find another method of adding axial base to the methane oxidation catalysts because our current method of using excess base may give a di-coordinated complex in which two base molecules occupy the two axial positions and leave no vacant site for oxygen binding. We expected that one of the axial base molecules would be released at the reaction temperature; however, the results did not indicate this to be the case.

EXPERIMENTAL DETAILS

Preparation of Magnesium Oxide Supported Ruthenium Monomer (RuMgO)

To a solution of Na(allyl)Ru(CO)3 (124 mg) in THF (30 mL) was added 5 g of LZ-Y52 zeolite that had been dried at 500°C for 6 h. The mixture was stirred for 16 h, and then the solvent was removed under reduced pressure at ambient temperature. The catalyst was activated at 200°C under helium flow before methane was introduced. Elemental analysis for ruthenium is 0.20%.

Preparation of Zeolite-Encapsulated Cobalt Schiff Bases

The zeolite-encapsulated catalysts [(1,2-diaminopropylene)bis-salicylideniminato]Co(II), CoSalPn-ZL, and [N,N'-(1,1,2,2-tetramethyl-ethylene)bis-(4-methoxysalicylideniminato)] Co(II), CoVan4TMen-ZL, were prepared by the same method. A mixture of aldehyde (salicylaldehyde or 4-methoxysalicylaldehyde), amine (1,2-diaminopropane or 1,1,2,2-tetra-methylethylene) and cobalt-exchanged zeolite (containing 4.76% cobalt ions) in a 2:1:1 molar ratio was heated in absolute ethanol to reflux for 16 h under inert atmosphere. The product was filtered and washed with dichloromethane until the washing was colorless. The unreacted cobalt ion was exchanged with sodium acetate in ethanol. The resulting zeolite, after filtration, was added to 1-methylimidazole and stirred overnight. The catalyst was filtered and then dried at 80°C under vacuum. Elemental analysis for cobalt was 0.70% in CoSalPn-ZL and 1.5% in CoVan4TMen-ZL.

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