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DIRECT CATALYTIC CONVERSION OF METHANE AND LIGHT HYDROCARBON GASES

Quarterly Report No. 10
Covering the Period January 1 to March 31, 1989

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INTRODUCTION AND SUMMARY

The United States will need to be able to convert coal to liquid fuels should current supplies of liquid fuels 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 dehydrocoupling methane. We will prepare the catalysts by reacting organometallic complexes of tranisition 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 the 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. Porphyrins 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 this reporting period, we have utilized samples of magnesia differing in their pretreatment temperature. Both the hydrido-ruthenium complex $H_4Ru_4(CO)_{12}$ and its reaction product with triethyl aluminum were reacted with these samples. The two ruthenium clusters are expected to react with the magnesia surface in different ways: by deprotonation of the hydride through an acid-base reaction with the basic surface, or by hydrolysis of the aluminum-carbon bond of the triethyl aluminum adduct. The concentration of hydroxyl groups on the magnesia surface able to hydrolyze the aluminum-carbon bond for immobilation should vary depending on the temperature of the pretreatment; the concentration of basic sites which can deprotonate the cluster should also vary with temperature. These differences were borne out by the experiment. We also compared the activity of two batches of $AlRu_4/MgO$ which had been synthesized at different times in the project. Both batches had approximately the same activity, but the newer batch had greater selectivity for C_{6+} hydrocarbons.

In the last reporting period, we had begun comparing the activity of the commercial hydrocarbon oxidation catalyst $(VO)_2P_2O_7$ (VPO) to the activity of the encapsulated and immobilized homogeneous catalysts we have been studying for the partial oxidation of methane. During this period, we finished this comparison with VPO and the result is it is much less active than the systems we have previously studied.

We also began work on a slurry reactor system in which to examine some of the more active oxidation catalysts we have discovered. The goal of the slurry reactor studies is to increase the selectivity for the partial oxidation products such as methanol. As part of this work, we synthesized for use in the slurry reactor two new batches of RuPC/Y, the most selective of the catalysts we have studied for the production of methanol. These two batches differed in their concentration of ruthenium present (the exact weight percent ruthenium awaits the results of elemental analysis).

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; 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.

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

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

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

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*SRI's study of the techniques for HDN catalysis, DOE Contract No. DE-FG22-85PC80906, and of FTS catalysis, DOE Contract No. DE-AG22-85PC80016.

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, $Fe(ally)_3$; 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).

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

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

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 automatic 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>in situ</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.

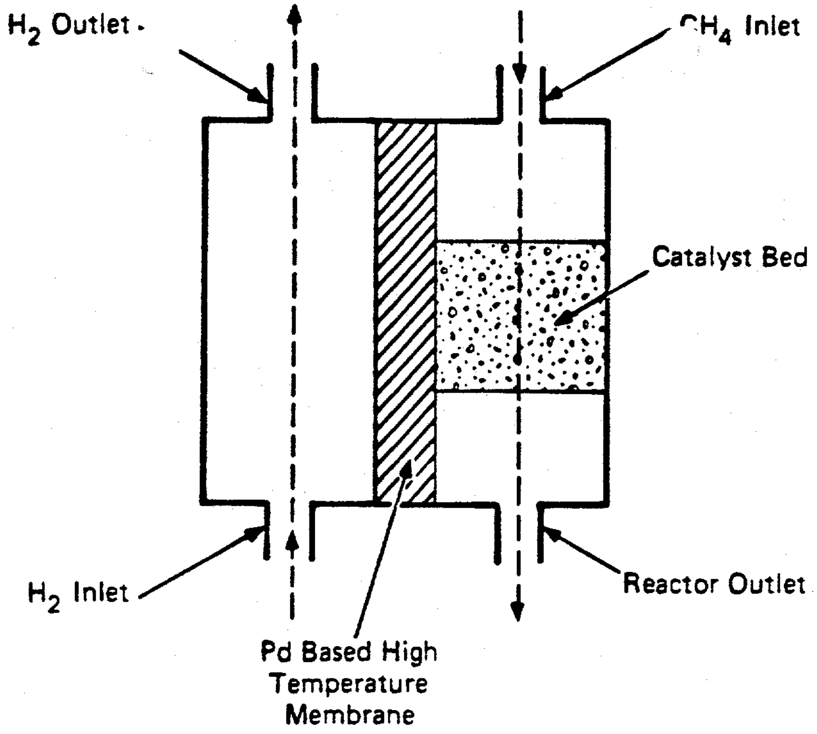

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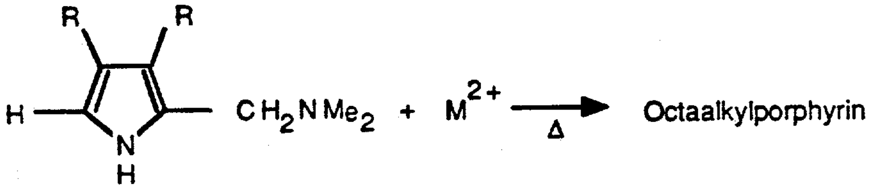
FIGURE 1 SCHEMATIC OF REACTOR WITH MEMBRANE FOR HYDROGEN CONTROL

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 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)

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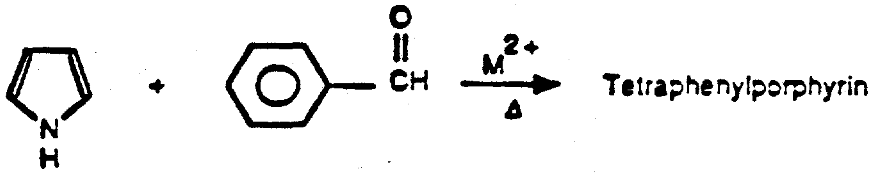
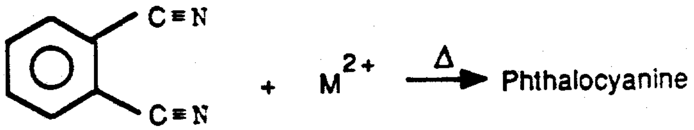
Alternatively, the cocondensation of pyrrole with benzaldehyde gives tetraphenylporphyrin [equation (5)].[30]



(5)

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



(6)

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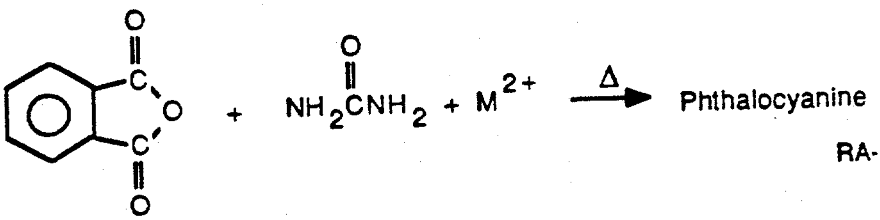
Alternatively, the condensation of phthalic anhydride and urea produces phthalocyanine [equation (7)].[31]



(7)

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Task 4: Testing of Methane Oxidation Catalysts

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 Quarterly Report Number 9, we reported on our first studies with a commercial hydrocarbon oxidation catalyst. We also began examining factors affecting the activity and selectivity of the immobilized aluminum-ruthenium clusters for the methane dehydrocoupling reaction. During this reporting period, we continued these studies.

One of the factors which may affect the activity of the $AlRu_4/MgO$ system in the methane dehydrocoupling reaction is the concentration of various surface groups on the magnesia. We dried batches of magnesia under two different conditions, and then supported both the hydrido-ruthenium cluster $H_4Ru_4(CO)_{12}$ and the aluminum-ruthenium cluster $(Et)_2AlH_3Ru_4(CO)_{12}$ on these two supports. As expected, the support treated at higher temperature showed more reactivity with the hydrido cluster, and less with the aluminum-ruthenium cluster. This reactivity was consistent with a higher concentration of hydroxyl groups. The acidic hydrido cluster reacts with basic sites on the surface such as oxide ions. Another factor that we have studied is the stability of the $AlRu_4/MgO$ catalyst with storage. Comparing the reactivity of a new and old batch of this catalyst demonstrated that the activity was about equivalent, but that the newer batch produced more higher hydrocarbons.

In our studies of the partial oxidation of methane, we began to assemble a slurry reactor in which to test some of the more active partial oxidation catlysts. We hypothesize that this slurry reactor will lead to more selective production of methanol in this oxidation reaction. We have synthesized two new batches of RuPC/Y (differing in ruthenium content) for use in this slurry reactor. This catalyst is the most selective for methanol of all the encapsulated or surface-immobilized phthalocyanines and porphyrins we have examined in the heterogeneous downflow reactors. We have also begun efforts to synthesize the perfluorinated analog of RuPC/Y.

We initiated studies of some commercial hydrocarbon oxidation catalysts to compare these catalysts to the encapsulated phthalocyanines and porphyrins we have synthesized and tested. The first of these commercial catalysts we examined is vanadyl pyrophosphate (VPO). During this reporting period we examined the reactivity of a VPO catalyst under a variety of gas mixtures ranging from our standard conditions (10:1

methane:oxygen) to the typical conditions used when VPO catalyzes oxidation of other light hydrocarbons (1:10 hydrocarbon:oxygen). The VPO is both less active and less selective than the catalysts we have been examining for the partial oxidation of methane.

Task 1: Synthesis of Methane Dehydrocoupling Catalysts

During this reporting period, we synthesized several new batches of $(Et)_2AlH_3Ru_4(CO)_{12}/MgO$ ($AlRu_4/MgO$) as a means of studying the effect of variables such as support pretreatment on the methane dehydrocoupling activity of this system. In the first batch synthesized in this period, the deposition solution was still colored after stirring for more than a day; this indicates that not all of the ruthenium complex reacted with the magnesia surface hydroxyls in the deposition reaction. The stoichiometry of this deposition was also very unusual; one-half the amount of ethane released in formation of the aluminum-tetraruthenium cluster (reaction 1) was released in the deposition reaction (reaction 2). Usually these amounts are equivalent.

$$Et_3Al + H_4Ru_4(CO)_{12} \longrightarrow EtH + Et_2AlH_3Ru_4(CO)_{12} \qquad (1)$$

$$Et_2AlH_3Ru_4(CO)_{12} + MgO \longrightarrow EtH + EtAlH_3Ru_4(CO)_{12}/MgO \qquad (2)$$

The observation that not all of the aluminum-ruthenium cluster reacted with the magnesia surface was somewhat suprising, since we had not encountered this difficulty before. After some thought, we decided that perhaps the difference was due to a change we had made in our pretreatment of the magnesia support. The original batch of magnesia was dried under vacuum at 375°C for ten hours before being brought into the dri-box and stored. More recent batches of magnesia were heated at 450°C for five hours under flowing nitrogen in order to remove extraneous water. This change was made for two reasons. One is that the flow apparatus was easier to set up and use with large amounts of magnesia. The second is that the higher temperatures and traces of oxygen present in the nitrogen would give a cleaner magnesia surface.

To test whether the pretreatment had any effect, a single batch of the aluminum-ruthenium cluster was synthesized. This was then redissolved in THF, and this solution split equally. Each portion was added to a sample of magnesia; one which had been pretreated at 375°C under vacuum, and the other which had been dried at 450°C under nitrogen. After stirring overnight, the sample depositing on the 450°C magnesia had more color in solution. This suggests that less of the cluster reacted with the magnesia surface in this sample. This is corroborated by the amount of ethane evolved during the two reactions (less from the 450°C MgO) and the amount of ruthenium complex recovered from THF washings after evaporation on the high vacuum line (60 mg vs 16 for the lower temperature MgO). We have sent out samples for elemental analysis to confirm the difference in ruthenium loading for these two samples. These results suggest that dehydroxylation is much more extensive at the higher temperatures, so that the amount of ruthenium that can be loaded by using hydroxyls as anchoring points is reduced. Removal of active surface hydroxyl groups by heating and elimination of water has long been known for other inorganic oxides such as alumina and silica.[32] With magnesia, removal of these surface hydroxyl groups is more critical for two reasons. The first is that magnesia samples generally have a much lower surface area than alumina or silica, so that in a given amount of oxide there is less surface to react with.[33] The second reason is that magnesia is a basic oxide[34], so that without the surface hydroxyls it will react with the hydrido-aluminum-ruthenium clusters in a different manner (acid-base interactions similar to what we used to immobilize the tetrasulfophthalocyanines on the surface of magnesia.)

Such reactivity has been proposed by Gates on a magnesia surface with ruthenium clusters,[35] after isolating the cluster anion $[H_3Ru_4(CO)_{12}]^-$ by extraction from the surface. We noted in Quarterly Report 8 that the reflectance IR spectrum of our Ru_4/MgO system is very similar to the spectrum reported by Gates for the $H_4Ru_4(CO)_{12}$/MgO system he studied.[35] This similarity prompted us to react some of the hydrido tetraruthenium complex directly with magnesia, rather than with triethyl aluminum and then magnesia, so that we could directly compare the systems through their metal loading, IR spectra, and their catalytic activity. In addition, if we are correct in our supposition that the higher temperature pretreated magnesia has fewer hydroxyls and is more basic, then the acidic hydrido-ruthenium cluster should react more extensively with this magnesia sample. As predicted, more solid was recovered from the reaction with the 375°C treated magnesia (the less basic sample). These samples have been sent out for elemental analysis, so that a direct measure of the ruthenium in the catalyst can be obtained. Combined with the results in the previous paragraph, this shows that the 375°C magnesia has more Bronsted acidity and less Bronsted basicity than the magnesia treated at 450°C. This difference in activity plays a major role in determining the amount of ruthenium on the surface. In the next period, we will examine its effect on the reactivity of these samples.

Task 2: Testing of Methane Dehydrocoupling Catalysts

Our major focus in this task during the past few months has been to raise the selectivity for C_{6+} hydrocarbons and use such systems for more extensive examination of the surface species present during reaction. In much of our work, we observed very little production of these hydrocarbons. Therefore one of the first things we did after the partial oxidation studies described below was to confirm our ability to observe C_{6+} production. We did this by saturating some magnesia with toluene in the dri-box and loading this sample into the reactor tube. The reactor was then mounted on the flow system, and the reactant gas mixture passed through. A large, broad peak was observed in the chromatogram. As the amount of toluene on the sample decreased, and the size of the chromatogram peak diminished, the retention time did not vary. We had been concerned that with small amounts of C_{6+} hydrocarbon generation, the C_{6+} peak may have shifted and been lost under some of the other peaks in the chromatogram. This experiment thus proves that the retention time remained constant, and that very small amounts of C_{6+} hydrocarbons can be observed during the reaction.

We then examined the activity of the $AlRu_4/MgO$ system for methane dehydrocoupling. One run was very interesting, in that we observed the production of both C_2H_4 and C_2H_6 at 750°C (in selectivity of 6.3 and 1.7% respectively). Slowing the flow rate from 50 to 20 ml/min at this temperature increased the selectivity of ethane to 5.3%, while that for ethylene decreased slightly to 5.9%. Production of C_3s was observed as well (0.2% selectivity) for the first time. The amount of methane conversion increased from 0.4 to 0.7%. When the solids were collected at the end of the reaction, the weight had almost doubled. Such a large increase suggests extraneous solids, and forcing acetone through the reactor under pressure did give a black suspension.

After thoroughly cleaning the tube reactor, the same $AlRu_4/MgO$ catalyst was reexamined. No hydrocarbons higher than C_2 were observed in this run. Slowing the flow as above increased the amount of methane conversion from 0.3 to 0.5%. The selectivity for hydrogen production increased to 97%, while the C_2 selectivity decreased from 4.3 to 1.6%. No C_3 or any higher hydrocarbon was observed. This raises the possibility that some carbon deposits may have a positive influence on the dehydrocoupling selectivity. Carbon has been proposed as the active surface in dehydrogenations such as ethylbenzene to styrene.[36]

We have synthesized several batches of $AlRu_4/MgO$ for examination in this project. During this quarter, we compared the activity of the oldest (over 15 months old) and newest (one month) batches. This comparison should give us an indication of the temporal stability of the $AlRu_4/MgO$ system. The old sample of $AlRu_4/MgO$ had very low activity. Less than 1% of the methane (0.04% at 550°C, 0.41% at 750°C) flowing through the catalyst reacted. The only products observed were hydrogen and C_2 hydrocarbons, and then only at 750°C (56 and 23% selectivity respectively). The new sample of the catalyst had similar activity (0.09 and 0.30% conversion of methane at 550 and 750°C). The only products observed at 750°C were hydrogen and C_2 hydrocarbons (60 and 6% selectivity). At 550°C, we observed C_{6+} production accounting for 92% of the methane reacted. This is a very encouraging result in terms of increasing the selectivity of the dehydrocoupling reaction to give gasoline-range hydrocarbons. The comparison of the activities for the old and new $AlRu_4/MgO$ systems shows that the activity of the system does not change much over time; some changes in the selectivity are observed. The reasons for this change in selectivity is unknown at present.

Task 3: Synthesis of Methane Partial Oxidation Catalysts

As part of our investigation into use of immobilized or encapsulated organometallic oxidation catalysts as catalysts for the selective partial oxidation of methane or other light hydrocarbons, we have also been investigating some heterogeneous catalysts commonly used in industry for various hydrocarbon oxidations. During the last reporting period, we synthesized a sample of vanadyl pyrophosphate $(VO)_2P_2O_7$ (VPO), which is used industrially to oxidize butane to maleic anhydride.[37] During this reporting period, we synthesized several more batches of VPO from the precursor compound $(VO)_2H_4P_2O_9$ using the same conditions described in Quarterly Report No. 9. As before, only VPO was observed by X-ray diffraction on the powder.

Tetraphenyl porphyrins (TPPs) with electron-withdrawing substituents on the phenyl rings have also been used as hydrocarbon oxidants in homogeneous systems.[38] Compared with unsubstituted TPPs, these catalysts retain their activity (at a higher level) for a much longer period of time.[39] The substituted analogs are also less heat sensitive than the unsubstituted TPPs and phthalocyanines (PCs). In previous Quarterly Reports (No. 3), we observed partial oxidation activity (formation of methanol) with three systems; RuPC, CoTPP, and MnTPP encapsulated in zeolite Y. When the temperature was raised to more than 425°C, these complexes decomposed. Use of porphyrins and phthalocyanines with electron-withdrawing substituents, such as fluorines in place of hydrogens (PFTPPs and PFPCs, respectively) would be expected to result in greater activity at the same temperatures with less decomposition. Since fluorine has the next largest covalent radius than hydrogen (0.72 and 0.37 Å),[34] the fluorinated TPPs and PCs should fit within the large cavity of zeolite Y, and so the complexes will still be encapsulated to prevent any inactivation by dimerization.

During the last reporting period, we first attempted the synthesis of the perfluorinated analog of RuPC encapsulated in Y type zeolite. Characterization of this species was difficult, in part because spectra and other such fingerprints of the fluorinated PCs have not been reported in the literature. During this period, we therefore synthesized CuPFPC by a literature method.[40] The procedure is similar to the synthesis of most phthalocyanines: the metal salt and tetrafluorophthalonitrile (a slight excess of the organic) were refluxed together in a high-boiling solvent (N-methyl pyrrolidone) for several hours. After cooling, the phthalocyanine was filtered and washed well. The spectra of this species can thus be used as means of determining our success in synthesizing encapsulated MPFPCs.

During this period, we began setting up a slurry reactor system (see below). The RuPC/Y system mentioned above has been our most successful system to date; 11.3% selectivity for the formation of methanol at 375°C (4.8% conversion of methane). It is therefore the first system we will examine in the slurry reactor, and so we synthesized a new batch of RuPC/Y. The ruthenium was first loaded into the zeolite by using a methanol solution of $Ru_3(CO)_{12}$ (Quarterly Report 1). Very little ruthenium was exchanged into the zeolite using this solution. In part this is due to the very low concentration of $Ru_3(CO)_{12}$ in methanol; it may also be due to the fact that the ruthenium must be oxidized to an ion before exchange can occur. We therefore synthesized another batch of ruthenium exchanged zeolite Y using $RuCl_2(DMSO)_4$[41] (DMSO is dimethyl sulfoxide) as the source of ionic ruthenium. This compound is soluble in water, so much higher concentrations of ruthenium can be exchanged in. Both batches of Ru/Y were dried under vacuum at 100°C after exchange. The synthesis of RuPC/Y was then carried out with both batches. The sample derived from Ru_3 was much lighter in color, thus confirming the lighter loading of ruthenium. Both samples gave identical UV spectra, so the same species (RuPC) is formed in both cases. Samples have been sent for elemental analysis so that the content of ruthenium will be known. It will be very interesting to compare the activity of these two samples. Herron has found that with encapsulated FePC/Y, the higher concentration (of iron) samples had <u>less</u> activity, not more, in a slurry oxidation of methylcyclohexane.[42] Is this true for the methane-oxygen system as well (gas phase as well as liquid phase)?

Task 4: Testing of Methane Partial Oxidation Catalysts

During the previous reporting period, we examined the vanadyl pyrophosphate VPO for activity in methane oxidation under our standard conditions (10:1 ratio of methane to oxygen, 375-450°C, 20 psi). Essentially no activity was observed. Industrially, this substance is used as a catalyst for the oxidation of butane to maleic anhydride.[37] In these reactions, the ratio of oxygen to butane is 10:1. This is the reverse of the conditions we have used in our methane oxidation experiments. We therefore conducted a series of experiments with VPO in which the ratio of methane:oxygen mixture passing through the catalyst at a flow rate of 100 ml/min was varied from 10:1 to 1:10. The temperature of the reaction was varied from 350 to 500°C. With a ratio of 10:1 methane:oxygen, only at 500°C was any methane oxidation activity observed (0.3% conversion). The only carbon-containing products observed were carbon monoxide and carbon dioxide; some water was observed, but could not be quantified. Similar results were observed with all of the other gas mixtures examined (2:1, 1:1, 1:2, and 1:10 ratios of methane:oxygen). The greatest amount of methane conversion (0.9%) occured at 500°C with a 1:1 ratio of methane:oxygen. These results demonstrate that the vanadyl pyrophosphate is much less active in oxidizing methane than the encapsulated or immobilized homogeneous catalysts we have been synthesizing. This lower activity is not accompanied by an increase in selectivity, as we have observed when lowering the temperature with our encapsulated catalysts. The reason for the lower activity of the vanadyl pyrophosphate in methane activation compared to butane may be due to the fact that the butane is large enough to be activated by two metal centers to give butenes, while methane is not large enough to span the distance between two metal centers.

During this period, we also began work on adapting another reactor system to operate as a slurry reactor with gas flow-through. We expect an increase in the selectivity for partial oxidation products of methane (especially methanol) by adjusting certain variables in the slurry reactor. Foremost among these is the choice of the solvent. The solvent for the slurry must be a substance which minimizes contact between a partial oxidation product such as methanol and the active oxidation catalyst. In the ideal case, methane would have a very high solubility in this solvent, while both oxygen and methanol would have minimal solubilities. Methane would then be present in the greatest concentration at the active site (the encapsulated complex). Once activated, it would react with the oxygen present in low concentration and over-oxidation to carbon dioxide would be diminished. Lessening the solubility of methanol would further enhance the selectivity for this partial oxidation product, since it would desorb from the solution before reacting further. We can test this last assumption by choosing solvents in which methanol is more soluble than methane. The solvent chosen for the slurry medium must also be one with a high boiling point, since the reaction will be conducted at temperatures greater than 200°C. With porphyrins and phthalocyanines encapsulated within the pores of zeolite Y, this solvent should also be too large to diffuse into the pore system. Then only the reagents (methane and oxygen) would have access to the active site on the interior of the zeolite, and side reactions such as oxidation of the solvent would be lessened. Our first choice as solvent is pyrene. The fused aromatic rings make it large and inflexible, so that it is unable to enter the pore structure of the zeolite. As a hydrocarbon, we anticipate methane being fairly soluble in it, while the more polar methanol is less soluble. Other possible choices are silicone oil and perfluoroethers, in which the carbon-fluorine bond would resist attack by the catalyst (much like in perfluorinated PCs and TPPs).

FUTURE WORK

Our work this quarter on the partial oxidation of methane with the vanadyl pyrophosphate catalysts examined whether this industrial hydrocarbon oxidation catalyst is active for methane oxidation. The results reported above show that VPO has minimal activity for methane oxidation under conditions where the encapsulated or immobilized catalysts we have been working with are active. Comparing the partial oxidation activity of two other known hydrocarbon oxidation catalysts (V_2O_5 on alumina and Pd on carbon) to our catalysts is a series of experiments we will attempt to carry out this next quarter. Synthesis of the perfluorinated analog of RuPC/Y is a more immediate goal, since this substituted phthalocyanine is expected to be both more stable and more active than the unsubstituted version, which is the best catalyst we have discovered to date. If time permits, we will also synthesize the tetra(pentafluorophenyl)porphyrins by a new method.

Our primary focus in the partial oxidation tasks for the rest of this project will be setting up and running the slurry reactor. We have already synthesized new batches of RuPC/Y to use in this reactor. Ideally, use of this slurry reactor will lead to more selective partial oxidations of methane by selective concentration (through differential solubility) of this hydrocarbon at the active site of the catalyst as well as lower temperatures of reaction. Another advantage of the slurry reactor is the quicker removal of the product methanol from the reactive center instead of letting it flow through the catalyt bed as it does in the flow reactors we have been using. In this next quarter, we will explore the activity of RuPC/Y in the slurry reactor as a function of the concentration of Ru (in the catalyst) and as a function of temperature.

If time permits, three other series of experiments would be of interest to do. One series is to study the variation of the oxidant cofed into the slurry reactor with the methane. Results in flow reactors suggest that oxidations with other oxidants, such as nitrous oxide[xh], is more selective for partial oxidations. Another set of experiments would be to vary the catalyst. Systems of interest would be some of the porphyrins we have studied previously, palladium or platinum tetrasulfophthalocyanine supported on magnesia, or some of the commercial hydrocarbon oxidants. In the third series of experiments, the hydrocarbon feed would be varied so that other light hydrocarbons such as propylene, butene, or ethane, would be introduced in combination with methane. Since many of the porphyrins or phthalocyanines we have immobilized or encapsulated have been examined as homogeneous epoxidation catalysts, we will study their reactivity with olefins in the slurry reactor to give epoxides.

For the methane dehydrocoupling studies, we intend to first compare the activities of the $AlRu_4/MgO$ and H_4Ru_4/MgO systems synthesized during this reporting period on the two different batches of magnesia, and see how the activity depends on the differences of the magnesia surface noted above. IR spectra and metal loading of these samples will also be compared. We plan to reexamine the behavior of the $AlRu_4$ and $AlFeRu_4$ systems on magnesia as they are heated under methane/argon in order to see if any of the changes we observe correlate with the reactivity of the catalyst. To do this we have obtained a tank of 40% methane in argon. Aside from changes in the carbonyl region, the region of C-H bond stretching (2700-3000 cm^{-1}) will also be monitored.

In addition to these studies, we will also be trying to maximize the selectivity for C_{6+} and C_2 products using the best catalysts we have previously reported (Ru_4/MgO, Ru_6/Al, and Ru_4/Y). Once we have this selectivity maximized, we will carry out Professor Lunsford's suggestion of trapping the surface carbon species with a flow of hydrogen. We have also begun to look into the possibility of using labeled methane (either ^{13}C or perdeuterated) as a similar type of probe. The labeled methane experiments will be especially helpful in demonstrating that the hydrocarbons we observe are arising directly from the methane we input. We could also examine the catalyst directly by solid state ^{13}C NMR and correlate the differences observed between dehydrocoupling catalysts and systems inactive as catalysts for this reaction with their activity. Comparison of the species obtained in the hydrogen pulse experiment with those obtained in less hydrocarbon selective system will provide information on which surface species lead to hydrogen and coke production, and which to higher hydrocarbons.

These experiments with labeled methane would be performed after this next quarter, since the time needed to obtain these chemicals would push these experiments back. There are several other experiments that, given enough time and money, we would like to perform in the area of methane dehydrocoupling catalysts. Prominent among these is to examine the use of traces of other hydrocarbons such as ethane (or functionalized hydrocarbons such as methyl bromide or acetone) as reaction initiators. These modifications of the feed gas would be expected to lead to greater selectivities for C_{6+} hydrocarbons. Several interesting results have been reported using a hydrogen plasma to initiate methane decomposition. We would like to set up a reactor incorporating a plasma torch to study how this modification changes the dehydrocoupling activity of the catalysts.

Another modification in our reactor we would like to study is the use of a hydrogen membrane to remove hydrogen from the system as it is formed.

REFERENCES

1. M. E. Dry and J. C. Hoogendoorn, Catal. Rev., 1981, 23, 265.
2. D. Hebdon and H.J.F. Stroud, "Coal Gasification Process," Chapter 24, in Chemistry of Coal Utilization, M. A. Elliot, Ed. (Wiley, New York, 1981), p. 1602.
3. M. E. Dry, "The Fischer-Tropsch Synthesis," in Catalysis Science and Technology, J. B. Anderson and M. Boudart, Eds. (Springer-Verlag, Berlin, 1981), p. 159.
4. D. L. King, J. A. Cusumano, and R. L. Garten, Catal. Rev., 1981, 23, 203.
5. H. C. Foley, S. J. D-Cani, K. D. Tau, K. J. Chao, J. H. Onuferko, C. Dybowski, and B. C. Gates, J. Am. Chem. Soc., 1983, 105, 3074.
6. T.-N. Huang and J. Schwartz, J. Am. Chem. Soc., 1982, 104, 5244.
7. Y. Iwasawa, T. Nakamura, K. Takamutsu, and S. Ogasawara, J.C.S. Faraday Trans. 1, 1980, 76, 939.
8. R. L. Burwell, Jr., and A. Brenner, J. Mol. Catal. 1975, 1, 77.
9. Y. Iwasawa, J. Mol. Catal. 1982, 17, 93.
10. Y. Yermakov, B. Kuznetsov, and A. Startsev, Kin. Catal. 1977, 18, 674.
11. Y. Yermakov and B. Kuznetsov, Kin. Catal., 1977, 18, 955.
12. B. N. Kuznetsov, Y. I. Yermakov, M. Boudart, and J. P. Collman, J. Mol. Catal., 1978, 4, 49.
13. Y. I. Yermakov, J. Mol. Catal., 1983, 21, 35.
14. M. Ichikawa, J.C.S. Chem. Comm., 1978, 566.
15. M. Deeba, J. P. Scott, R. Barth and B. C. Gates, J. Catal., 1981, 71, 373.
16. J. M. Basset and A. Choplin, J. Mol. Catal., 1983, 21, 95.
17. J. P. Candlin and H. Thomas, "Supported Organometallic Catalysis" in Homogeneous Catalysis II, D. Forster and J. F. Roth, Eds., Adv. Chem. Series 1974, 132, 212-239.
18. Y. I. Yermakov, Catal. Rev.-Sci. Eng., 1976, 13, 77.

19. Y. I. Yermakov, B. N. Kuznetsov, and V. A. Zakharou, "Catalysis by Supported Complexes," Vol. 8, Studies in Surface Science and Catalysis (Elsevier, Amsterdam, 1981).

20. B. C. Gates and J. Lieto, Chemtech, 1989, 10, 195.

21. G. Meyers and M. Hall, Inorg. Chem., 1984, 23, 124.

22. B. C. Gates and J. Lieto, Chemtech. 1980, 10, 248.

23. D. D. Whitehurst, Chemtech, 1989, 10, 44.

24. D. C. Bailey and S. H. Langer, Chem. Rev., 1981, 81, 109.

25. M. Kaminsky, K. J. Yoon, G. L. Geoffroy, and M. A. Vannice, J. Catal., 1985, 91, 338.

26. R. B. Calvert and J. R. Shapley, J. Am. Chem. Soc., 1977, 99, 5225.

27. F. A. Coton and G. Wilkinson, Inorganic Chemistry, Vol. 4 (Wiley, New York, 1982).

28. B. J. Wood, U.S. Patent No. 3,770,797,973.

29. N. Herron, C. A. Tolman, and G. D. Stuckey, Abstracts 189th ACS National Meeting, Miami Beach, Florida.

30. K. M. Smith, Porphyrins and Metalloporphyrins (Elsevier, Oxford, 1975).

31. F. H. Moser and A. L. Thomas, The Phthalocyanines, Vol. II (CRC Press, Boca Raton, FL, 1983).

32 Chapter 1 in Tailored Metal Catalysts, edited by Y. Iwasawa, D. Reidel Publishing Company, New York, 1986.

33 Typical values for magnesia are 25-30 m^2/g, while for alumina or silica surface areas are tyically ten times greater.

34 Table of Periodic Properties of the Elements, Sargent-Welch Scientific Company.

35 S. Uchiyama and B.C. Gates, J. Cat. (1988) 110, 388.

36 L.E. Cadus, L.A. Arrua, O.F. Gorriz, and J.B. Rivarola, Ind. Eng. Chem. Res. (1988) 27, 2241 and references therein.

37 B.K. Hodnett, Catal. Rev.-Sci. Eng., (1985) 27, 373.

38 P.S. Traylor, D. Dolphin, and T.G. Traylor J. Chem. Soc. Chem. Comm. (1984) p. 279.

39 C.K. Chang and F. Ebina J. Chem. Soc. Chem. Comm. (1981) p. 778.

40 F.H. Moser and A.L. Thomas, Ed. The Phthalocyanines, CRC Press, Boca Raton, 1983, Vol. II, p. 11.

41 B.R. James, E. Ochiai, and G.L. Rempel Inorg. Nucl. Chem. Letters (1971) 7, p. 781.

42 N. Herron, G.D. Stucky, and C.A. Tolman J. Chem. Soc. Chem. Comm. (1986), p. 1521.