DOE/PC/90011--T9

March 10, 1989

Direct Catalytic Conversion of Methane and Light Hydrocarbon Gases

Quarterly Report No. 9
Covering the Period October 1 to December 31, 1988

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ACQUISITION & ASSISTANCE DIV.

Contract No. DE-AC22-86PC90011
SRI Project No. 2678

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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 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.

During this reporting period, we completed our IR spectroscopic examination of the Ru_4/MgO and $FeRu_3$/MgO systems under nitrogen and methane by examining $FeRu_3$/MgO under methane. This system behaved quite differently than the same system under nitrogen. Under methane, only one very broad peak is observed at room temperature.

Upon heating, the catalyst transformed so that by 300°C, the spectrum of $FeRu_3/MgO$ under methane was the same as that of Ru_4/MgO. This suggests that methane promotes the segregation of the metals in the mixed metal system. The differences in catalytic activity between the $FeRu_3/MgO$ and Ru_4/MgO systems may then be due to the presence of IR transparent species such as iron ions which cause different nucleation in the ruthenium clusters.

We examined several systems for activity in the methane dehydrogenation reaction. We are focusing on systems which produce C_6 hydrocarbons since this is the most useful (and interesting) product. These systems all displayed low activity so that the amount of hydrocarbon product is very low. Some C_6 hydrocarbon is observed over zeolite supports, but its production ceases after the first few hours of reaction. We prepared a new system, Ru_4 supported on carbon, and examined its reactivity. Its activity was very low and in fact the carbon support had the same level of activity.

We synthesized four new systems for examination as catalysts in the partial oxidation of methane. Three of these (PtTSPC/MgO, PtTSPC and PdTSPC on carbon) are analogs of PdTSPC/MgO. This system is of interest because we have observed the production of ethane from methane oxidation over PdTSPC/MgO at relatively low temperatures and we wished to explore its generality among close analogs. We also synthesized a vanadyl pyrophosphate, $(VO)_2P_2O_7$ (VPO), which is a catalyst for the oxidation of butane to maleic anhydride, in order to compare its reactivity to our methane oxidation catalyst.

We then examined these systems, as well as PdTSPC/MgO, for activity in oxidizing methane. Our goal was to optimize production of hydrocarbons from these systems. The major product in all cases was carbon dioxide. Ethane was observed with PdTSPC/MgO and PtTSPC/MgO; in the latter case, it was observed only at higher flow rates and a greater methane:oxygen ratio, conditions designed to minimize the complete oxidation of methane to carbon dioxide. The phthalocyanines supported on carbon are less active than when supported on magnesia. VPO was inactive for methane oxidation under our 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; 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 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)].

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

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

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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).

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

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

The carbonyl clusters include $H_2Ru_3(CO)_{11}$, $H_2Ru_4(CO)_{13}$, and $H_2Ru_6(CO)_{18}$ for Ru and the mixed Fe/Ru clusters $H_2FeRu_2(CO)_{11}$, $H_2RuFe_2(CO)_{11}$, $H_4Ru_3Fe(CO)_{12}$, and $H_4Ru_2Fe_2(CO)_{12}$.

Characterizing the surface-confined complexes is the key to understanding their stability and activity.

Task 2: Testing of Methane Reforming Catalysts

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 in situ stabilized Pd membrane to control the H_2 partial pressure[28] (see Figure 1). Variables to be studied will also include space velocity of methane, temperature, hydrogen pressure, and hydrogen flow rate.

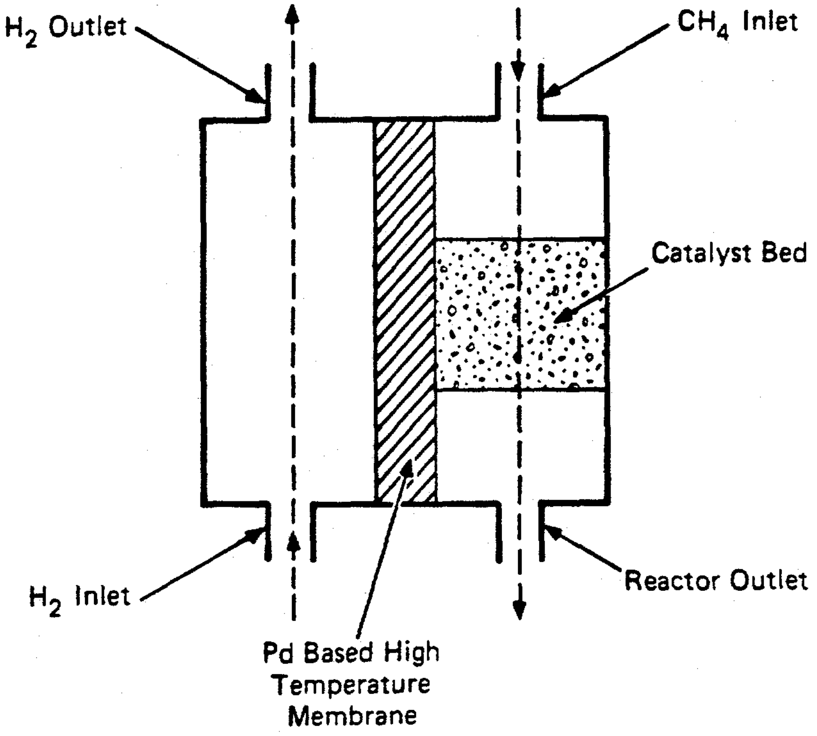

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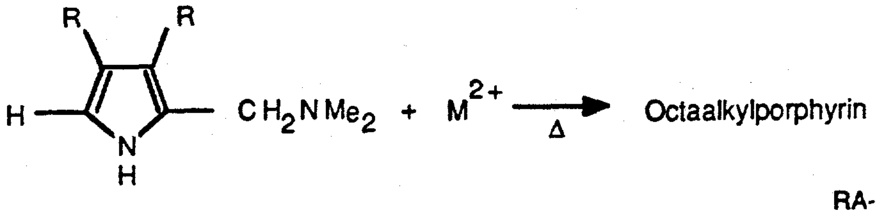
FIGURE 1 SCHEMATIC OF REACTOR WITH MEMBRANE FOR HYDROGEN CONTROL

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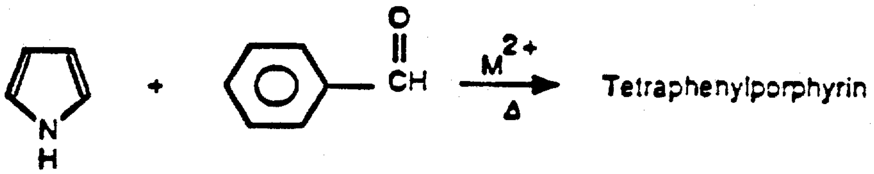
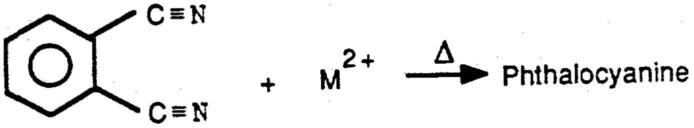
Alternatively, the cocondensation of pyrrole with benzaldehyde gives tetraphenylporphyrin [equation (5)].[30]



(5)

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



(6)

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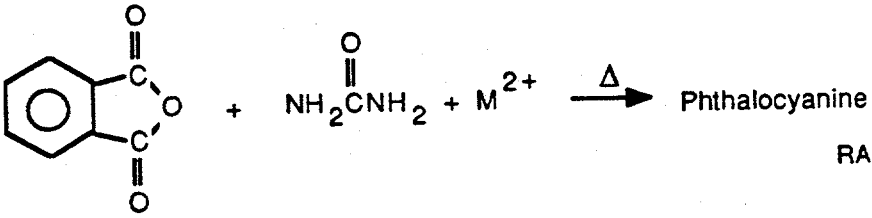
Alternatively, the condensation of phthalic anhydride and urea produces phthalocyanine [equation (7)].[31]



(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 8, we began to investigate the origin of the greater activity of $FeRu_3/MgO$ compared to Ru_4/MgO in the methane dehydrogenation reaction. We observed that under nitrogen, the mixed metal cluster decarbonylated at much lower temperatures than the tetraruthenium cluster. The presence of the iron has therefore affected the reactivity of the cluster. In this reporting period, we examined the behavior of the mixed metal system under methane. We also examined several supported cluster systems for activity in dehydrogenating methane. Under Task 3, we synthesized several new systems which are analogs of PdTSPC/MgO. We examined their reactivity; the platinum analog converted more methane than the palladium compound on both carbon and magnesia. We observed some hydrocarbon production with PtTSPC/MgO under conditions designed to minimize production of carbon dioxide.

As part of our work under Task 1, we examined the behavior of $FeRu_3/MgO$ under methane/argon. The room temperature IR spectrum differed from that previously observed under nitrogen for the same complex. As we heated this sample under methane, the spectrum changed so that it resembled that observed with Ru_4/MgO; two peaks at 2030 and 1950 cm^{-1}. Under nitrogen, $FeRu_3/MgO$ was completely decarbonylated by this temperature. Upon further heating, the spectrum observed for $FeRu_3/MgO$ changed in an identical way as observed upon heating Ru_4/MgO at the same temperature. The presence of methane has therefore promoted the segregation of the metals in the iron-ruthenium system, so upon heating a ruthenium species is formed on the surface that resembles the species formed from a ruthenium only system. The greater activity of the $FeRu_3/MgO$ system in reacting with methane may be due to the presence of species such as iron ions which cause different nucleation in the ruthenium clusters on the magnesia surface.

In other work under Task 1, we synthesized some carbon supported ruthenium clusters using Ru_4 and Ru_6 clusters. We then examined a Ru_4/C system for activity in dehydrogenating methane; it displayed no greater activity than the carbon support alone. We also examined several other supported cluster systems in which we had previously observed C_{6+} production. In these experiments, much lower activity for methane dehydrogenation was observed. Both freshly synthesized and older samples had low activity, so ageing of the catalysts does not appear to be the sole cause of this decline.

Under Task 3, we synthesized a new batch of PdTSPC/MgO, as well as three new supported catalysts: PtTSPC/MgO, PtTSPC/C, and PdTSPC/C. We also synthesized an industrial hydrocarbon oxidation catalyst, vanadium pyrophosphate, which is used to oxidize butane to maleic anhydride. These compounds were all examined for their activity in oxidizing methane to ethane or methanol. No methanol was observed; ethane was observed with PdTSPC/MgO and PtTSPC/MgO. The platinum systems were more active for conversion of methane than the corresponding systems with palladium but the selectivity to hydrocarbon was much lower.

Task 1: Synthesis of Methane Reforming Catalysts

During this reporting period, we prepared a new catalyst by reacting $H_4Ru_4(CO)_{12}$ with triethyl aluminum, then reacting the resulting complex with Mogul L, a carbon black used in making inks. Mogul L is an acidic carbon black, so the surface contains functional groups such as carboxylic acids, phenols, and hydroxyl groups. The acidity of this carbon black is much less than an inorganic oxide such as alumina. Before use it was dried at 120°C under vacuum to remove physisorbed water. The solution did not decolorize after stirring overnight with the carbon, so not all of the ruthenium complex reacted with the carbon surface. The carbon was therefore washed with THF (to remove physisorbed ruthenium cluster) in the dri-box and dried under vacuum before use.

We have previously reported the behavior of Ru_4/MgO and $FeRu_3$/MgO under nitrogen in the DRIFT cell as the samples were heated. We also studied the behavior of Ru_4/MgO under 5% methane/argon. We have been studying these catalysts by infrared spectroscopy as a means of explaining the greater reactivity of the mixed metal cluster for methane dehydrogenation which we have observed. In this period, we studied the behavior of $FeRu_3$/MgO under the methane/argon mixture as it was heated. A comparison of the spectra of $FeRu_3$/MgO under nitrogen and methane is shown in Figure 2. Under nitrogen, we observe three peaks at 2030, 2005, and 1985 cm^{-1}; the peak at 1985 cm^{-1} is the most intense. Shoulders are observed at 2050 and 1940 cm^{-1}. Under methane, a very large absorption is observed centered at about 2005 cm^{-1}; there is a great deal of fine structure on this peak, which suggests that a large number of species have been formed. This spectrum differs from that observed by Basset et al.[32] with $H_2FeRu_3(CO)_{13}$ on magnesia. The broad absorption is reminiscient of a feature observed by Guczi in the interaction of these mixed metal clusters with hydrated alumina.[33] This absorption is attributed to the absorption by mobile subcarbonyls which arise from the decomposition of the cluster.

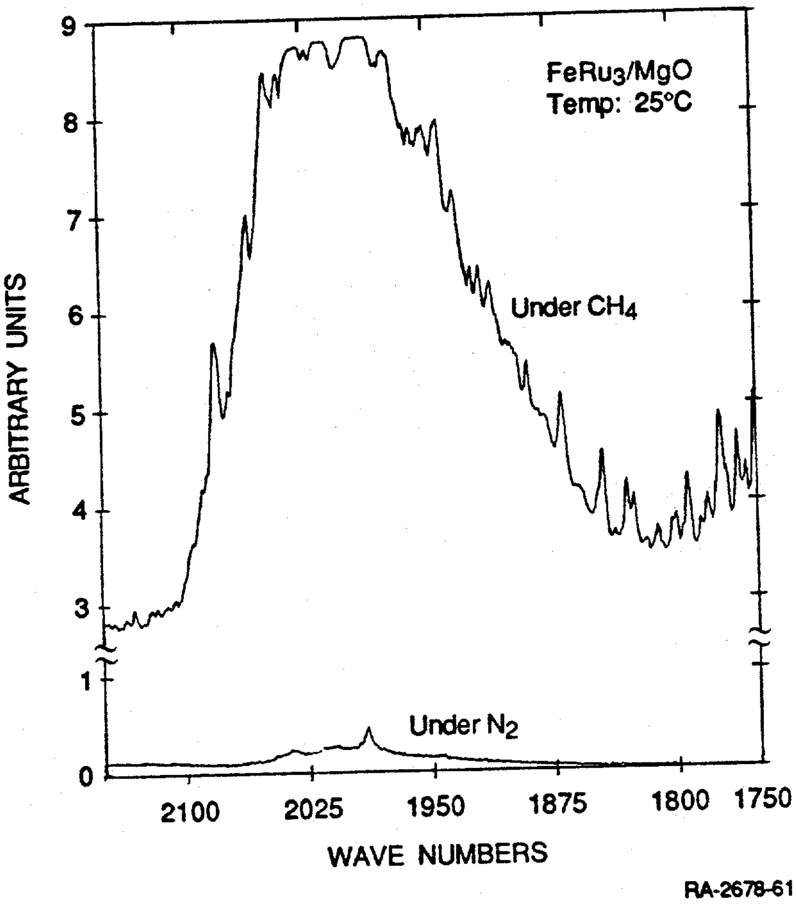

Figure 2. Comparison of $FeRu_3$ cluster on MgO under CH_4 and N_2.

When $FeRu_3/MgO$ is heated under nitrogen, the absorption due to carbonyl bands practically disappears between 100 and 200°C. By 300°C, no absorption bands are observed (Figure 3). Under methane, peaks are observed in the carbonyl region for this system. At 300°C, a peak is observed at 2030 cm^{-1}, along with a broader peak at about 1950 cm^{-1}. Both the peak positions and relative intensities match the spectrum observed for Ru_4/MgO (Figure 4) under nitrogen or methane. This indicates that the mixed metal cluster has decomposed and segregated into separate iron and ruthenium species. Guczi has observed a similar segregation on alumina.[33] Upon further heating, the species derived from $FeRu_3/MgO$ behaves exactly like Ru_4/MgO. The higher wavenumber band has disappeared by 400°C, and the lower wavenumber band has slightly shifted to lower wavenumbers (Figure 5). By 600°C, no bands are observed in the carbonyl region. The difference in behavior of the $FeRu_3/MgO$ system under nitrogen and methane is very suprising, especially since we have not observed such differences with the Ru_4/MgO system. Apparently the decomposition of the $FeRu_3/MgO$ system gives some very active ruthenium species which can interact with methane and promote the further segregation of the two metals, so that the $FeRu_3/MgO$ system resembles Ru_4/MgO. The iron present in this system may undergo a disproportionation reaction to give some volatile iron carbonyls and some iron ions which can act as nucleation centers for ruthenium clusters. These clusters may have different morphologies, and thus different catalytic properties, from those observed in the Ru_4/MgO system.

Task 2: Testing of Methane Reforming Catalysts

Our work under this task focused on the production of C_{6+} hydrocarbons. We did this for three reasons. One is that the selective production of such hydrocarbons from methane dehydrocoupling would be very useful. Another reason is that we want to examine such a system's long-term activity for the production of these hydrocarbons. A third reason is that we wished to carry out an experiment suggested by Professor Lunsford. He suggested that when higher hydrocarbons are being produced at a steady rate, the reactant gas should be switched to hydrogen and the carbon products that desorb be observed. The hydrogen should act as a trap for any carbon species on the surface of the catalyst and so provide information about the carbon-containing intermediates on the surface during the reaction. When compared to the products arising from a non C_6 producing system, this experiment gives us information on the species leading to such higher hydrocarbon formation.

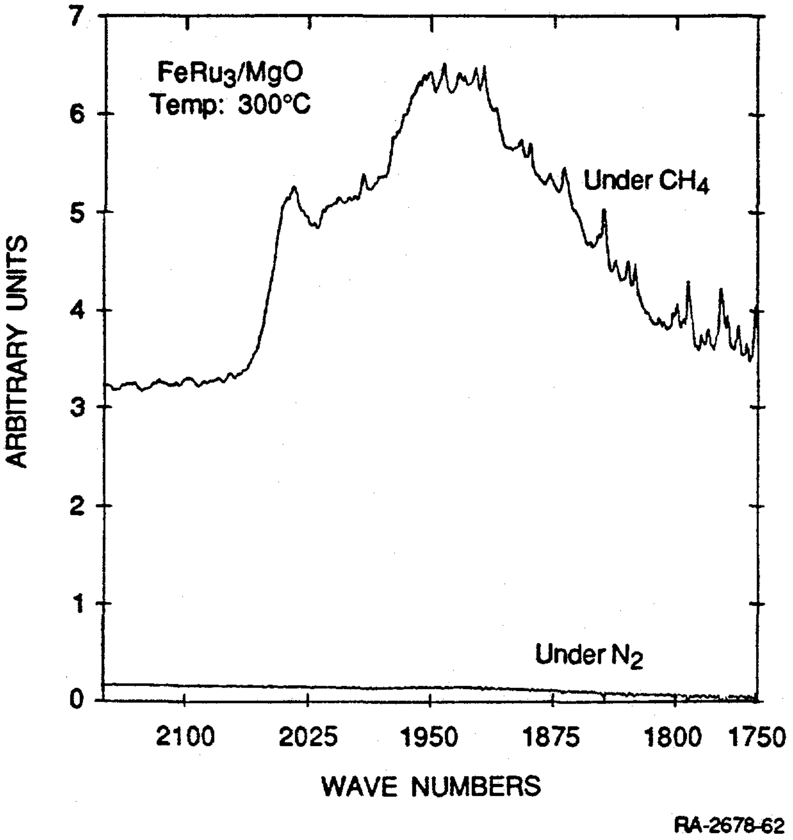

Figure 3. Comparison of $FeRu_3$ cluster on MgO under CH_4 and N_2.

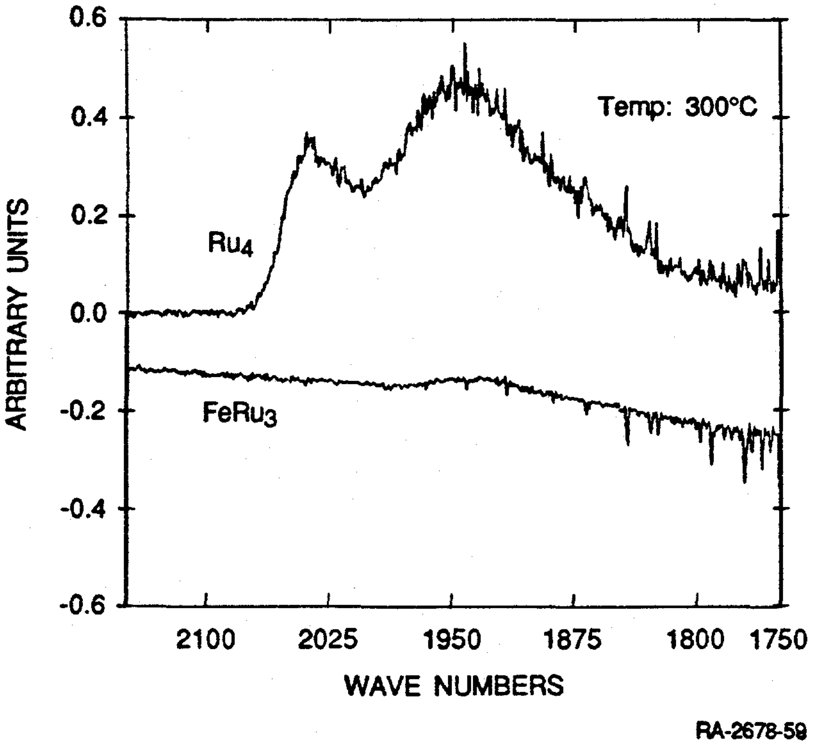

Figure 4. Comparison of Ru_4 and $FeRu_3$ clusters on MgO under N_2.

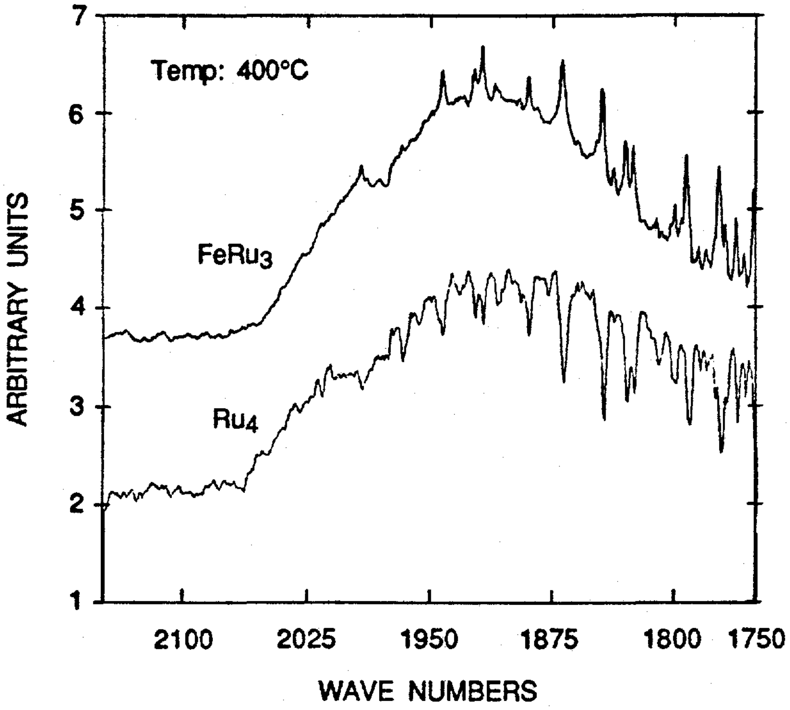

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Figure 5. Comparison of Ru_4 and $FeRu_3$ clusters on MgO under CH_4.

After recalibrating the GC at a higher pressure we examined four systems. C_6 production had previously been observed at 750°C with these four systems (Ru_4/MgO, Ru_6/Y, Ru_4/Y, and Ru_6/MS) with selectivities ranging from 2.5 to 49.2%. In the experiments conducted during this reporting period, C_6 production was observed only at the beginning of the reaction with Ru_6/MS and Ru_4/Y. After four or five hours on stream, these hydrocarbons were no longer observed. The main products observed were hydrogen and C_2 hydrocarbons. The conversion of methane in these experiments is very low (Table 1). Our inability to observe consistent C_{6+} production is in all likelihood related to these low conversions. The reasons for this decline in performance are unclear at present. These experiments were conducted at the pressures and flow rates previously studied, so that leaks in the reactor system are no longer a problem. The transfer lines from the reactor to the GC are all heated to 110°C, so the products should be volatilized into the GC. Another possibility is ageing of the catalysts. Such a phenomenon has been observed by Zecchina with $Ru_3(CO)_{12}$ on hydrated alumina.[34] The system changed upon exposure to the atmosphere at room temperature from a simple physisorbed Ru_3 species to one which consisted of two peaks at 2072 and 2005 cm^{-1} (much like we have observed for Ru_4/MgO). When heated, all of the samples decarbonylated to give the same spectrum. These workers attribute the ageing to oxygen and/or water exposure. Our samples have been stored in the dri-box, so exposure to air and water in storage have been minimized. The ageing must therefore occur by some other method. What this process is that leads to lower conversions is unknown at present. Further work to obtain steady C_{6+} hydrocarbon production is in progress.

Table 1: Production of Hydrocarbons By Methane Reforming Catalysts[a]

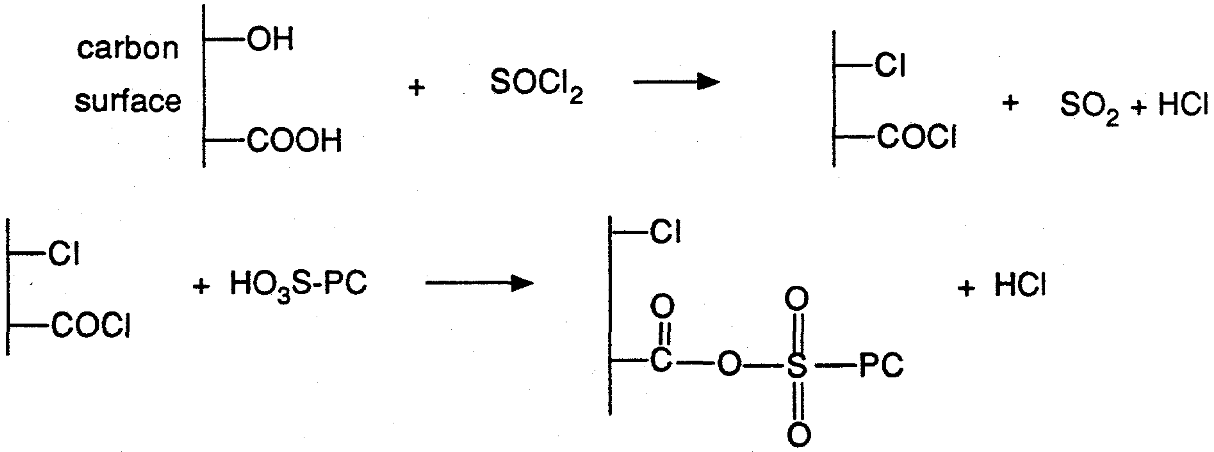
Catalyst	Methane Conversion(%)	Selectivity(%)[b] H_2	C_2	C_6
Ru_4/MgO	0.4	199	3.3	--
Ru_6/Y	0.25	109	--	2.4
Ru_6/MS	0.48	16.5	1.7	--
Ru_4/Y	0.25	0	--	--

a Conditions; 750°C, 150 psi, 50 ml/min
b Selectivity to hydrocarbons are based on carbon number.

We also tested the Ru_4/C system synthesized in Task 1 during this reporting period. Very low conversions of methane were observed. The only products are hydrogen and C_2 hydrocarbons. The same level of activity is observed with the carbon support alone. This dehydrogenation by unsupported carbon is quite unusual. Coke on alumina has been studied as a catalyst in dehydrogenations such as the conversion of ethylbenzene to styrene.[35] The alumina promotes the formation of the coke which is the active catalyst for ethylbenzene dehydrogenation.

Task 3: Synthesis of Methane Oxidation Catalysts

During the previous reporting period, we synthesized PtTSPC as part of our effort to examine the reactivity of PdTSPC/MgO analogues. These analogues would enable us to determine how widespread the low temperature production of ethane from methane by this family is. During this period, we reacted the PtTSPC with magnesia to form PtTSPC/MgO. We also reacted this complex with carbon (Mogul L). The carbon was pretreated by refluxing with thionyl chloride, which converts all of the carboxylic acid groups on the surface of the carbon into acid chloride groups; in addition, some surface hydroxyl groups will also be converted to chlorides. This carbon was next refluxed with benzene twice to remove any occluded thionyl chloride. It was then dried in vacuo before use. The acid form of PtTSPC was then added to the carbon in a DMF/DMSO solution, so that an ester like compound is formed between the sulfonic acid and the acid chloride, and the suspension allowed to stir overnight. The solvent was removed under vacuum, since the carbon particles were too fine to separate by filtration or centrifugation. After drying the black solid was stored in a vial outside the dri-box. PdTSPC was supported on carbon by the same methods. Second batches of both PtTSPC and PdTSPC supported on magnesia were synthesized.



We also synthesized a vanadium pyrophosphate complex, $(VO)_2P_2O_7$ (VPO), which is active in the oxidation of butane to maleic anhydride.[36] We are interested in comparing the activity of this hydrocarbon oxidation catalyst with our phthalocyanine and porphyrin systems in the oxidation of methane. The vanadium compound is synthesized in two steps. The precursor complex $(VO)_2H_4P_2O_9$ is synthesized by slowly adding V_2O_5 to an 80°C solution of hydroxylamine in phosphoric acid, then, after stirring for one hour, slowly removing the solvent. A small amount of water is added and refluxed, after which the reaction mixture is filtered. The resultant green complex gave an X-ray powder pattern identical to the one in the literature for $(VO)_2H_4P_2O_9$.

VPO is prepared from this precursor by dehydration at elevated temperatures. Our conditions for this dehydration were slightly different from those in the literature;[36] our nitrogen flow was slower (60 vs 100 ml/min), and the solid was kept at 570°C for a longer period of time (4 hours vs 2). The literature conditions gave only amorphous products in our attempts. The synthesis of VPO was confirmed by comparison of its X-ray powder pattern to that published in the literature. Heating the $(VO)_2H_4P_2O_9$ to greater than 600°C gave a different complex, whose X-ray powder pattern did not match any vanadium phosphate complex thus far identified in the literature.

Task 4: Testing of Methane Oxidation Catalysts

During this reporting period, we calibrated the GC for two different flow rates (50 and 100 ml/min). The response factors are slightly different for these two flow rates. Both internal (relative to nitrogen) and external response factors have been calculated from these standardizing runs. When the standard gas mixture was heated to 375°C, no change was observed in the composition of the mixture. Heating to 425°C did not change the hydrocarbon balance, but did change the amounts of hydrogen, carbon dioxide, oxygen, and carbon monoxide in the gas stream. Thus, the output of carbon dioxide at this higher temperature is a combination of direct production from methane and secondary production from carbon monoxide.

Since the observation of ethane as a product in the low temperature oxidation of methane by PdTSPC/MgO, we have been concentrating on synthesizing analogues of this system. We had earlier examined two complexes (NiTSPC and PdTCPC) which had been supported on magnesia. We reexamined these two systems, and confirmed that they are inactive for the oxidation of methane. During this period, we synthesized three other analogs (PtTSPC/MgO, PdTSPC/C, and PtTSPC/C) and examined their activity for the partial oxidation of methane. The results are collected in Table 2. Only the palladium systems produce C_2 hydrocarbons in this reaction. The platinum systems are much more active than the corresponding palladium compound; for example, PdTSPC/MgO at 425°C oxidizes 2.0% of the methane, while the platinum complex oxidizes 4.4% at the same temperature. Essentially all of the oxygen was consumed during this reaction by PtTSPC/MgO. At higher flow rates (100 ml/min) this difference is more pronounced; at 375°C, the palladium system oxidizes 0.1% while the platinum system oxidizes 3.0% of the methane (consuming 70% of the oxygen). The main product in all cases is carbon dioxide; carbon monoxide is generally produced in much smaller quanitities. Only the palladium system produces ethane; we have observed selectivities as high as 3.6%. The platinum system produces only carbon oxides and water. When PtTSPC and PdTSPC are supported on carbon, these systems are less active than the corresponding magnesia based species; for example, PtTSPC/C at 425°C oxidizes 0.2% of the methane. Thus the support plays an important role in this reaction; the nature of this role is unclear at this point. It could be a support effect on the metal complex, or a direct effect in activating the methane. Carbon dioxide is again the main product. On carbon, PdTSPC does not produce any ethane.

We attempted several modifications of the reaction conditions with PtTSPC/MgO in an attempt to slow down the oxidation of methane and produce some hydrocarbons. Doubling the flow rate of the reactant gas mixture still produced only carbon oxides. We exchanged the steel reactor tube we had been using for one of titanium metal, since Dr. M. Wax had reported in the recent symposium on methane activation that this tubing was less reactive in secondary reactions.[37] Again only carbon oxides are observed. We doubled the ratio of methane to oxygen from 10 to 20:1; this lowered the methane conversion. At 350°C, no hydrocarbons were observed. Finally at 335°C, we observed some ethane (0.4% selectivity) and traces of a C_3 product.

We also examined the VPO catalyst for activity in methane oxidation. We are interested in the activity of VPO since we want to compare the activity of the systems we have developed with some industrial systems. We observed no reaction over the temperature range of 350-450°C. In this temperature range, the catalyst is active for butane oxidation.[38] This reaction is usually run with an excess of oxygen relative to hydrocarbon, whereas the conditions we have been using for methane oxidation are the reverse of this.

Table 2
Methane Oxidation Reactions[a]

Catalyst	Temp (°C)	CH_4 Conv. (%)	Selectivity(%)[b] CO_2	CO	C_2	H_2O
NiTSPC/MgO	375	no rxn.				
	425	no rxn.				
PdTCPC/MgO	375	no rxn.				
	425	no rxn.				
$(VO)_2P_2O_7$	350	no rxn.				
	375	no rxn.				
	400	no rxn.				
	425	no rxn.				
	450	0.005	19.1	3.7	--	65.9
PdTSPC/MgO	375	no rxn.				
	425	2.0	77.9	2.4	3.6	36.3
PtTSPC/MgO	375	1.8	22.7	2.6	--	2.6
	425	4.4	52.8	1.5	--	36.6
PdTSPC/C	350	no rxn.				
	375	no rxn.				
	400	no rxn.				
	425	0.2	105	3.2	--	--
	450	0.4	93.3	14.9	--	obs.
PtTSPC/C	350	no rxn.				
	360	no rxn.				
	375	no rxn.				
	400	0.2	30.6	0.9	--	--
	412	1.0	50.6	22	--	20.0
	425	3.5	35.0	3.4	--	26.4
PtTSPC/MgO[c]	375	3.0	13.8	1.7	--	27.7
	350	1.0	3.2	4.9	--	3.7
	360	1.1	31.9	--	--	--
PdTSPC/MgO[c]	350	0.1	16.6	--	--	--
	375	0.1	19.3	--	--	15.0
	400	0.4	20.1	--	1.8	21.0
	425	1.6	29.6	1.9	1.1	15.3
	400	1.7	9.8	0.9	13.0	32.2
	375	0.5	--	--	1.4	--
PtTSPC/MgO[c,d]	350	1.0	29.6	7.1	--	obs.
	335	1.0	27.2	7.7	0.4	obs.
PtTSPC/MgO[e]	350	3.4	38.9	4.1	--	29.9
	335	0.5	52.9	--	--	5.3
c	335	0.2	30.6	--	--	59.0
	375	1.2	47.9	0.6	--	27.6
f	350	0.5	50.7	1.9	--	11.1
	375	3.9	35.3	3.7	--	34.4

a. Standard conditions- flow= 50 ml/min; 10:1 ratio methane:oxygen; 2 g catalyst; P= 20-30 psi
b. Selectivity based on carbon number
c. Flow= 100 ml/min; P= 30-40 psi
d. 20:1 ratio methane:oxygen
e. Flow= 200 ml/min; P= 50 psi

FUTURE WORK

The IR studies we have carried out in the last two reporting periods have yielded some very interesting results. This quarter we examined the behavior of $FeRu_3/MgO$ under methane/argon. The spectra at higher temperatures (300°C) for this system were similar to the those of Ru_4/MgO under either methane or nitrogen. In contrast, $FeRu_3/MgO$ under nitrogen behaved very differently; at 300°C, no peaks are observed in the carbonyl region of the infrared spectrum. Obtaining the spectra of other ruthenium clusters and mixed metal clusters (such as Ru_6 or $CoRu_3$) on magnesia under these conditions would be of interest to see if they all transform into the same species as Gates has proposed for ruthenium clusters under Fischer-Tropsch type conditions.[39] We will also attempt to reexamine the tetraruthenium and iron triruthenium clusters on magnesia under methane in order to observe any changes in the C-H or carbonyl regions due to reaction with methane. These new clusters will also be of interest since we can study the effect of the metal composition and the beginning cluster geometry on the systems' methane dehydrogenation activity. We have already shown that the mixed metal $FeRu_3$ cluster is more active for methane dehydrogenation than the corresponding Ru_4 complex on both acidic (zeolite) and basic (magnesia) supports. Other metal complexes with the same nuclearity which are of interest include Ru_2Fe_2, $CoRu_3$, and a second type of Ru_4 and $FeRu_3$ cluster.[40-43] We intend to support the most interesting of these clusters on carbon (Mogul L first, then mol sieve carbon) and zeolite as well as magnesia, which would provide data about the effect of the support in these reactions.

Our studies of the methane dehydrogenation reaction will be directed toward maximizing 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. Comparison of these species with those obtained in a less hydrocarbon selective system will provide information on which surface species lead to hydrogen and coke production, and which to higher hydrocarbons. In addition, we plan to examine the most selective of these catalysts in a modified system containing a hydrogen selective membrane. Removal of the hydrogen produced in the dehydrogenation of methane should drive the equilibrium toward more hydrocarbon product.

In our studies on the methane oxidation reaction, we first intend to examine the effect of changing the methane:oxygen ratio on the reactivity of the vanadyl pyrophosphate compound used in butane oxidation. Once methane oxidation is observed, we can then examine one of the porphyrin or phthalocyanine systems we have synthesized under the same conditions so that we can make a valid comparison of their activity. We also intend to reexamine the reaction of PtTSPC/MgO with a 20:1 ratio of methane to oxygen, and confirm the production of C_2 and C_3 hydrocarbons in this system.

We also intend to begin studies with some of the more active methane oxidation catalysts (such as PtTSPC/MgO, RuPC/Y, and CoTPP/Y) in a slurry reactor under flow-through conditions. By using a solvent for the slurry in which both methanol and oxygen are relatively insoluble, we hope to increase the selectivity for partial oxidation products. This solvent must also be unable to penetrate the zeolite pore system, so that it will not compete with methane for coordination to the metal. Construction of this new reactor system will begin in the next quarter.

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