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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, much of our effort focused on investigating the stability of the methane reforming catalysts (Task 2) with respect to storage time. Many of these catalysts demonstrated lessened activity when they were reexamined up to 18 months after they ere first synthesized and tested. We also synthesized and tested two new phthalocyanines supported on magnesia (MgO) for examination in the methane oxidation reaction.

We reexamined many of the hexaruthenium and tetraruthenium clusters which had been supported on zeolite Y, zeolite 5A, alumina or magnesia. These reexaminations were conducted at relatively slow flow rates (15 ml/min), since previous studies had shown that the lower flow rates maximized the conversion of methane in this reaction. In every case, the catalyst exhibited diminished activity compared to the earlier runs. In addition, the selectivity of the cata lysts changed as well; relatively less C_2 and no C_6 was observed in the reactions conducted during this reporting period. Since the question of the stability of the catalysts during storage is quite important, we intend to explore this in more detail in subsequent periods.

In the previous technical report (Quarterly Report 6), we reported that palladium tetrasulfophthalocyanine (PdTSPC) supported on MgO exhibited exceptional activity in the methane oxidation reaction; it produced ethane at much lower temperatures than previously reported in the literature. We synthesized two close analogues of this compound, one with a different metal (nickel) from the same family as palladium, and the other with a different substituent (carboxylic acid rather than sulfonic acid) on the phthalocyanine ring. Both of these complexes were supported on magnesia, and tested for activity. The nickel complex displayed some activity, producing only carbon dioxide and water.

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)].

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

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

Specifically, we are attempting to generate surface-confined metal complexes by using equation (1). We 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).

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

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

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 insitu 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.

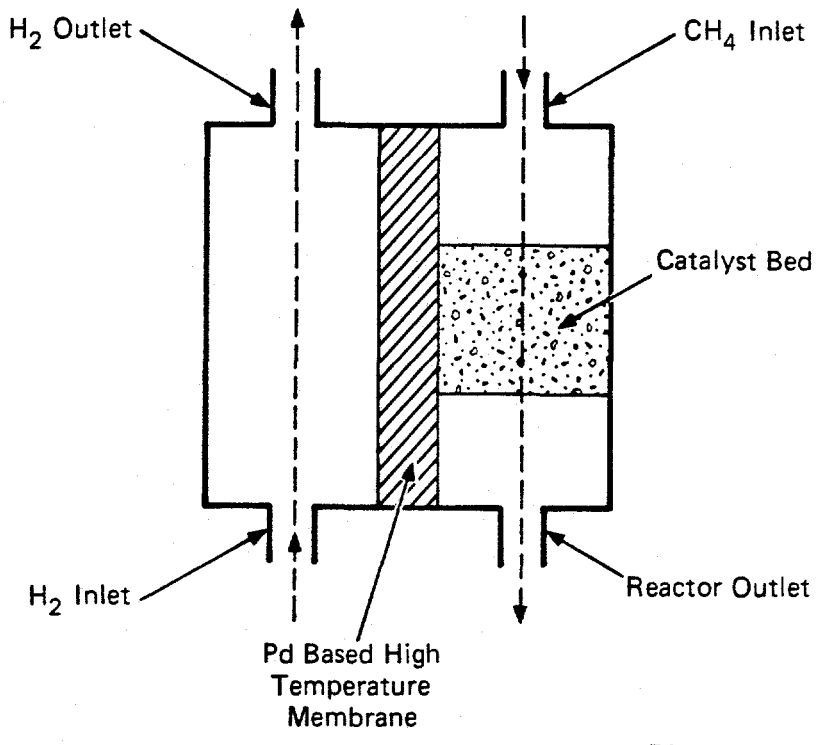
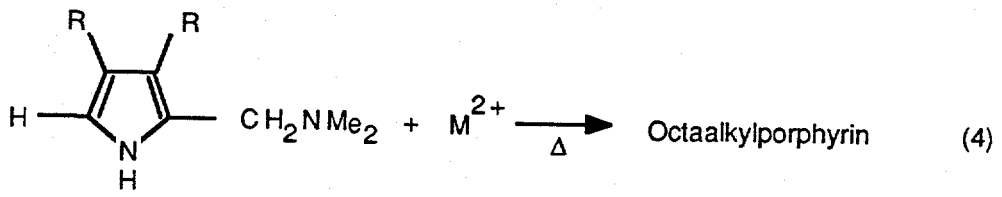


FIGURE 1 SCHEMATIC OF REACTOR WITH MEMBRANE FOR HYDROGEN CONTROL

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.



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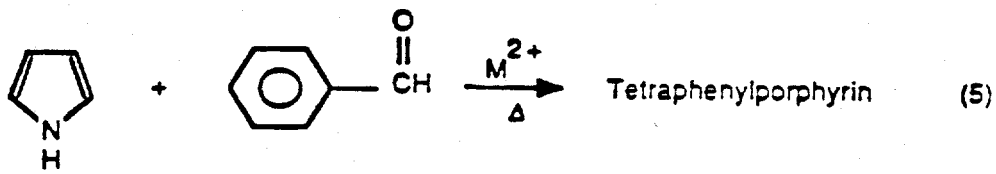
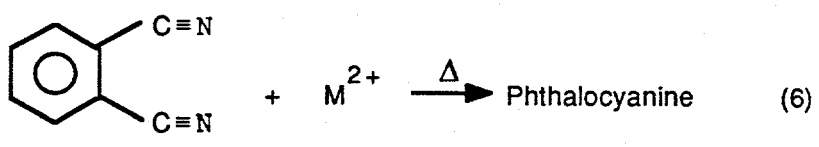
Alternatively, the cocondensation of pyrrole with benzaldehyde gives tetraphenylporphyrin [equation (5)].[30]



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



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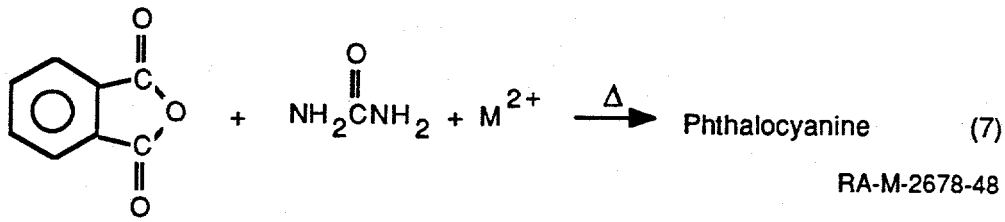
Alternatively, the condensation of phthalic anhydride and urea produces phthalocyanine [equation (7)].[31]



Task 4: Testing of Methane Oxidation Catalysts

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

In Quarterly Report Number 6, we reported the results of using several magnesia supported metal tetrasulfophthalocyanine complexes as methane oxidation catalysts. In most cases (metal being Fe, Co, Cu, Mn, and Mo) no activity beyong that of underivatized magnesial was observed. For two metals (Ru and Pd), some activity beyond that of the support was observed. In both cases, the majority of the carbon containing product was carbon dioxide; with palladium, ethane was also observed in small amounts. The production of ethane at such low temperatures (375°C) in the methane oxidation reaction is unprecedented. We also observed that our supports (zeolite Y and magnesia) were catalyzing the decomposition of our primary reaction product.

In this reporting period, we have followed up on this observation. We synthesized two close analogues; one in which the acid substituent on the phthalocyanine ring was changed, and the other in which palladium was substituted by nickel, a metal from the same family in the periodic table. The nickel complex displayed some activity for methane oxidation, but did not produce any ethane as its palladium cogener had. The newly synthesized palladium complex did not display any activity for methane oxidation. Thus, at present, the PdTSPC/MgO system is unique in its ability to produce ethane while oxidizing methane.

We also reexamined the catalytic activity of several of the supported ruthenium clusters in the methane dehydrogenation reaction as a test of the catalysts' stability in storage over time (up to 18 months in some cases). Both hexaruthenium and tetraruthenium clusters were studied in this regard. The results indicate that the activity of the supported complexes declined while in storage for all of the cases thus far studied. The best case was Ru_6Y, which retained 30% of its original activity. The selectivity for the reaction products changed as well. No C_6 product was observed in any of the runs during this reporting

period. In most cases, the selectivity for C_2 products and hydrogen also declined.

Task 2: Testing of Methane Reforming Catalysts

We reexamined the catalytic ability of the following systems in the methane dehydrogenation reaction; Ru_4 on MgO, alumina (Al), and zeolite 5A (5A), and Ru_6 on zeolite Y (Y) and 5A. Our primary purpose in performing this reinvestigation was to check the stability of the catalysts over long periods of storage. Another reason for carrying out these reactions was to check som e of our earlier reactions, in which an internal standard was not present and so the error in the measurement of the hydrocarbon present was greater. The reactions were run under conditions designed to maximize the conversion of methane; thus, relatively slow flow rates (15 ml/min) and high temperatures (750°C) were used. Under such conditions, the selectivity for hydrocarbon product is not necessarily maximized. We chose to emphasize activity over selectivity in these studies because we believed that t he activity would be a better measure of the stability of the catalyst systems.

The results from the runs carried out in this reporting period, as well as data from comparable runs with the same catalyst carried out in earlier quarters are collected in Table 1. These results clearly demonstrate that the supported ruthenium complexes are less active now in dehydrog enating methane than when originally studied. The three supported tetraruthenium systems all showed large declines in activity; the residual activity ranged from 0.1 to 10%. No hydrocarbons greater than C_2 were observed at any point during the reactions. The selectivity for the production of hydrogen and C_2 products was also greatly reduced for these systems. Thus, much of the methane that is apparently reacting is unaccounted for. With the low conversions of methane we are observing in these reac tions, the fluctuations in the amount of methane present are of the same order of magnitude as the amount of methane actually reacting; thus our error in determining the amount of methane reacting is very large in these cases.

Table I

Ru SUPPORTED CATALYSTS FOR METHANE REFORMING REACTIONS

Catalyst	% CH_4 conv.	% sel H_2	% sel C_2	%sel C_6	GHSV
$Ru_4/5A$[a]	0.45	18.54	0.8	n.o.[b]	4600
$Ru_4/5A$[c]	4.9	146.6	3.5	n.o.[b]	31000
Ru_4/Al[a]	0.02	0	0.3	n.o.[b]	7100
Ru_4/Al[c]	10.1	78.6	1.6	n.o.[b]	47500
Ru_4/MgO[a]	0.26	10.36	0.1	n.o.[b]	6400
Ru_4/MgO[d]	4.0	42.8	6.9	49.2	2100
Ru_6/Y[a]	1.12	189.4	7.9	n.o.[b]	4600
Ru_6/Y[c]	3.6	161.9	3.6	10.0	16000
$Ru_6/5A$[a]	0.07	0	0.1	n.o.[b]	4600
$Ru_6/5A$[c]	5.6	192.8	1.0	14.8	16000

[a]This period.
[b]n.o.= not observed.
[c]from Quarterly Report 2.
[d]from Quarterly Report 5.

The two hexxaruthenium cluster systems studied as a test of their stability also showed a loss of activity for methane dehydrogenation. The cluster supported on 5A sieves was essentially inactive when reexamined, while the Ru_6/Y cluster retained 30% of its original activity ov er the 18 months of storage. No C_6 product was observed. The selectivity for both hydrogen and C_2 were somewhat greater in the more recent run. The amount of hydrogen produced suggests that coke was formed in this reaction, which accounts for practically all of the rest of the converted methane (assuming that each carbon atom in the coke

accounts for two molecules of hydrogen). The causes of the diminished activity of the complexes is unclear at this time. This could be due to a change in the acid ity of the zeolite support, degradation of the ruthenium cluster, or the slower flow rates used in the more recent experiments. We are currently in the midst of synthesizing fresh samples of these systems for testing so that we can evaluate these hypotheses.

We also performed an experiment in which we examined the steadiness of a ruthenium cluster's activity for methane dehydrogenation over a longer reaction period. During this run, we encountered many problems with our GC sampling system, so that this experiment needs to be repeated. Qualitatively, the activity of the Ru_6/Y system appeared to be stable (hydrogen and C_2s were produced) over the 120 hours we followed this reaction at 750°C. We submitted samples of this catalyst before and after this long run for elemental analysis. The amount of ruthenium present was essentially constant (0.25 to 0.28% Ru). The amount of carbon and hydrogen declined upon reaction; from 8.30 to 3.44% for carbon, and from 2.38 to 0.64% for hydrogen. The decline in the amount of carbon, along with the small amount of hydrogen present, suggests that, after the original carbonyls and ethyl groups have been removed, relatively little coking has occured on the remaining metal atoms. This can be attributed to the ability of the hexaruthenium cluster to pass into the interior pores of the zeolite, where they will be isolated, and thereby stabilized, from other clusters as they are reduced to the small metal particles. These small metal particles are less likely to promot e coke formation.[32]

During this reporting period, we examined the behavior of the Ru_6/Y catalyst by infrared spectroscopy (IR) while it was heated under flowing nitrogen. By obtaining the spectra of the catalysts as they are heated under an inert gas (and then a 10% methane/helium mixture), we hope to be able to correlate the changes we observe on heating with the reactivity of the supported complexes. In the case of the hexaruthenium complex supported on zeolite Y, the IR spectrum at room temperature

showed three features in the carbonyl region; a doublet around 2000 cm^{-1} and a shoulder around 1770 cm^{-1}. In the alkane region (3000 cm^{-1}), we could not separate the C-H stretches of interest from the overtones of some of the zeolite cage frequencies. A different data workup technique is available which would enable us to carry out such a separation, and which we have begun to use routinely. Between 300 and 400°C, the carbonyl peaks observed at room temperature disappeared except for a weak sh oulder at about 2050 cm^{-1}. Above 600°C, the IR spectrum was essentially featureless above 1400 cm^{-1}. Thus, the hexaruthenium cluster, at these higher temperatures, has essentially decomposed.

Task 3: Synthesis of Oxidation Catalysts for Methane

In the previous reporting period, we prepared several metal tetrasulfophthalocyanines (TSPC), which were then supported on magnesia. The sulfonic acid substituent was incorporated to enhance the binding of the phthalocyanine to the basic magnesia surfa ce. Of the complexes we prepared, PdTSPC displayed the greatest reactivity, converting the most methane to mostly carbon dioxide and some ethane. The production of ethane at such low temperatures in the oxidation of methane was unprecedented according to the literature (Table 4 in Quarterly Report 6), so that we wished to explore the reactivity of other magnesia supported phthalocyanines for the production of ethane.

During this reporting period, we prepared two analogues of PdTSPC, and supported them both on magnesia. In one case, we changed the sulfonic acid substituent on the phthalocyanine ring for a carboxylic acid, and retained palladium as the central metal ion (giving PdTCPC). In the other case, we kept the sulfonic acid substituents, but exchanged the palladium for nickel (giving NiTSPC), the metal directly above palladium in the periodic table. Both systems were synthesized according to the previously reported techniques (Quarterly Report 6), and then supported on magnesia. We submitted a sample of the PdTCPC/MgO system for elemental analysis, and found that the loading of palladium was very low (0.076%). This is even lower than the PdTSPC system

(0.18%), which was the lowest of the TSPC complexes analyzed (Quarterly Report 6, Table 2). The lower loading of the PdTCPC could be due to the weaker acidity of carboxylic acid groups, which would interact less strongly with the basic surface of the magnesia. The amount of carbon, hydrogen, and nitrogen present in the PdTCPC/MgO sample was much higher than would be associated with the palladium alone, so that it appears that most of the phthalocyanine on the surface has been demetallated. This was also observed in the PdTSPC and FeTSPC systems, although to a much lesser extent. Such demetallation is most likely to occur on the acidification step just before deposition on the magnesia.

We had previously (Quarterly Report 3)studied the use of tetraphenylporphyrin (TPP) complexes entrapped in zeolite Y as oxidation catalysts. Of these, the ru thenium complex was the most active, but produced only carbon dioxide. The cobalt and manganese complexes were less active, but produced methanol as well as the deep oxidation product carbon dioxide. These complexes decomposed at temperatures greater than 450°C. The fluorinated analogues (PFTPP), in which all the hydrogens on the four phenyl rings are replaced by fluorines, are also known hydrocarbon oxidation catalysts. Under these oxidizing conditions, the fluorinated species are more stable than the TPP species.[33] Because of these advantages, we decided to examine the PFTPP complexes of several metals in the methane oxidation reaction.

The synthetic procedure we used for the synthesis of the PFTPP entrapped within the zeolite Y pores was based on our previously reported procedure for the synthesis of the TPP species (Quarterly Report 3). However, upon mixing the pentafluorobenzaldehyde and pyrrole, an exothermic reaction took place to give a black, tarry solid. This was added to the refluxing acetic acid suspension of zeolite Y, and then the mixture refluxed further for a few hours. After cooling and filtering, we dissolved away the zeolite by dissolution in concentrated sulfuric acid, and examined this solution by UV-vis spectroscopy. The spectrum did not display any trace of the chromophore identified with PFTPP. Efforts to modify this synthesis are currently underway.

Task 4: Testing of Methane Oxidation Catalysts

As mentioned above, we have reported previously on the utility of a series of magnesia-supported metal-TSPC complexes for the oxidation of methane. Of those tested, PdTSPC was not only the most active, but also was the only one to produce ethane. We therefore synthesized two analogues of this complex (see above), and tested them during this reporting period. The PdTCPC/MgO catalyst was run at 375°C at a GHSV of 5300 h^{-1} using a 10:10:1 mixture of methane:nitrogen:oxygen. Essentially no reaction was observed under these conditions. The NiTSPC/MgO catalyst was examined under similar conditions. The flow rate of the reactant gases were very low, which proved to be due to a leak in the downflow reactor apparatus (identified in subsequent reactions). Qualitatively, we did observe some methane oxidation by this nickel complex, producing only water and carbon dioxide. The experiment will be repeated so that we can make valid comparisons to the other oxidation catalysts. Thus far, therefore, the PdTSPC/MgO system is still unique in its ability to produce ethane under the r elatively mild conditions of methane oxidation we employ.

FUTURE WORK

The work we have carried out during this reporting period suggests that the synthesis of the various ruthenium clusters on zeolite Y, zeolite 5A, and alumina be repeated so that we can compare the reactivity and selectivity of these new batches with those which have been stored (under nitrogen in a dry box) for long periods of time. These complexes will also be attached to two different types of carbon, which as a neutral support should catalyze fewer secondary reactions than the acidic zeolites or basic magnesia.

Aside from the tetra- and hexaruthenium clusters, mixed metal clusters of similar nuclearity are also of interest. We have already shown that the mixed metal $FeRu_3$ cluster is more active for methane dehydrogenation than the corresponding Ru_4 complex. Other metal complexes with nuclearity of four which we plan to synthesize are Ru_2Fe_2, $CoRu_3$ (two types), another type of Ru_4 and $FeRu_3$ cluster, and $Ru_nO\ s_{4-n}$.[34-37] Examining complexes with the same metal core, but different bonding in that core, will enable us to investigate the effect of this difference (if any) in the methane dehydrogenation reaction.

In Task 3, our efforts will be directed toward synthesizing two types of compounds, analogues of the PdTSPC/MgO system that gave ethylene and fluorinated analogues of the TPP and PC complexes studied earlier. We have already begun synthesizing analogues of PdTSPC/MgO by varying the metal or the substituent on the phthalocyanine ring. The effect of the support on the PdTSPC catalysts will also be studied by changing the support to zeolite Y or carbon. The second type of compound we have begun preparing are fluorinated analogues of the underivatized TPP and PC complexes we examined earlier (Quarterly Reports 1 and 3). The advantages of these fluorinated species over the underivatized analogues are twofold; they are generally more stable

under oxidizing conditions; and they are also more heat-stable. Our first attempts in this area have been reported above (for PFTPP).

We intend to examine the Ru_4 and $FeRu_3$ complexes supported on magnesia by IR spectroscopy as they are heated under flowing gases (either an inert atmosphere, or with a small percentage of methane). Such a comparison should give us data on why the mixed metal cluster is active at far lower temperatures than the tetraruthenium cluster. The spectra of a particular cluster (e.g. Ru_6) on different supports would also be of interes t in terms of comparing the reactivity of these systems.

We are currently working on converting our analysis technique to one which is not dependent on the size of the sample taken for GC analysis. Using a standard gas mixture, we intend to investigate the sensitivity of this technique to changes in temperature, flow rate and pressure within the system. This should enable us to reduce the variation in the amount of methane measured, and thereby increase the accuracy of our calculations for the amount of methane converted and the selectivity of the various products.

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, 1980, 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, 1980, 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. Somorjai, G.A., Chemistry in Two Dimensions: Surfaces, Cornell University Press, Ithaca, NY, 1981, p. 486.

33. Patricia S. Traylor, David Dolphin, and Teddy G. Traylor, J. Chem. Soc. Chem. Comm. (1984), page 279-280.

34. Gregory L. Geoffroy and Wayne L. Gadfelter, J. Am. Chem. Soc. 99, 7565, (1977).

35. Paul C. Steinhardt, Wayne L. Gladfelter, A. Dale Harley, Joseph R. Fox, and Gregory L. Geoffroy, Inorg. Chem. 19, 332, (1980).

36. Wayne L. Gladfelter, Gregory L. Geoffroy, and Joseph C. Calabrese, Inorg. Chem. 19, 2569, (1980).

37. Alak A. Bhattacharyya, Colleen C. Nagel, and Sheldon G. Shore, Organometallics 2, 1187, (1983).