DOE/PC/90011--T8

March 1, 1989

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DIRECT CATALYTIC CONVERSION OF METHANE AND LIGHT HYDROCARBON GASES

Quarterly Report No. 8
Covering the Period July 16 to Sept. 30, 1988

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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 requires two steps: 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 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 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 stabilizes the highly dispersed catalysts and the acidic nature of the zeolite is likely to contribute to the dehydrocoupling 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 enhances the stability and reactivity of the catalysts and discourages 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 presented our results in two papers at the methane activation symposium held in conjunction with the Los Angeles ACS meeting. We investigated the behavior of some of our catalysts under working conditions using diffuse reflectance fourier transform infrared spectroscopy (DRIFT). Two catalysts ($FeRu_3$ and Ru_4 on magnesia) were examined under nitrogen, and the Ru_4/MgO system was examined under a methane/argon mixture. We synthesized ruthenium clusters supported on carbon as catalysts for methane reforming and new phthalocyanines to be used as catalyst precursors for oxidizing methane to methanol.

The Ru_4 and $FeRu_3$ complexes supported on magnesia exhibited very different behavior in the DRIFT cell when heated under nitrogen. The $FeRu_3/MgO$ system was completely decarbonylated by 400°C, while spectrum of the Ru_4 system displayed carbonyl peaks until the temperature rose to over 600°C. The Ru_4/MgO system behaved almost identically under methane/argon as it did under nitrogen in the carbonyl region. In the C-H region of the spectrum (2800-3100 cm^{-1}), peaks were observed under methane but not under nitrogen. The intensity of these peaks did not vary with temperature.

We synthesized new catalysts by supporting the Ru_4 and Ru_6 clusters on carbon. Both acidic zeolites (Type Y or 5A) and basic magnesia (MgO) have been observed to react with hydrocarbons at high temperatures; these reactions generally lead to coking, then deactivation of the catalyst contained on these supports. We expect carbon to be a truly inert support.

We had previously 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 the platinum analogue of this complex and will support it on magnesia for investigation in the next reporting period. We also wish to investigate the role of the magnesia support in this reaction by supporting the PdTSPC on other supports and have synthesized a Pd-exchanged Y type zeolite to be used to synthesize PdTSPC on Y-zeolite.

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)].

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

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).

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

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

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.

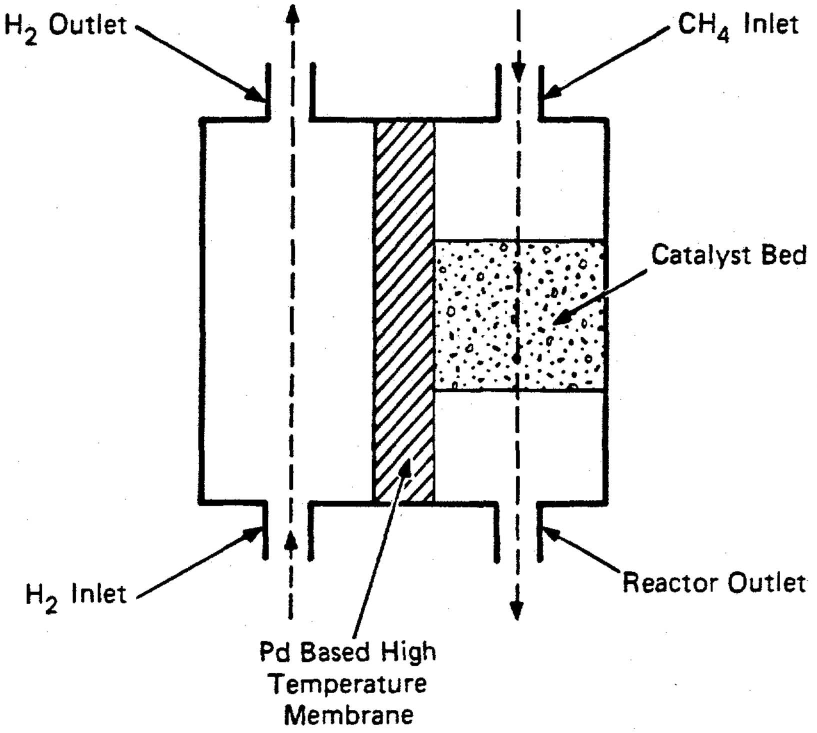

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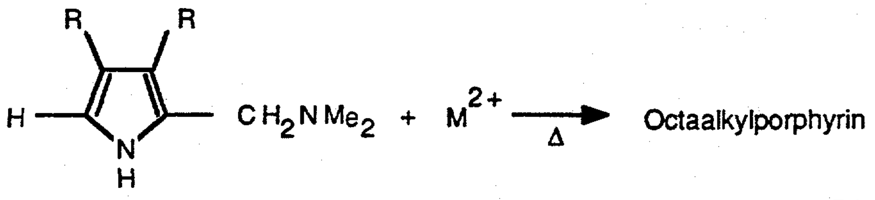
FIGURE 1 SCHEMATIC OF REACTOR WITH MEMBRANE FOR HYDROGEN CONTROL

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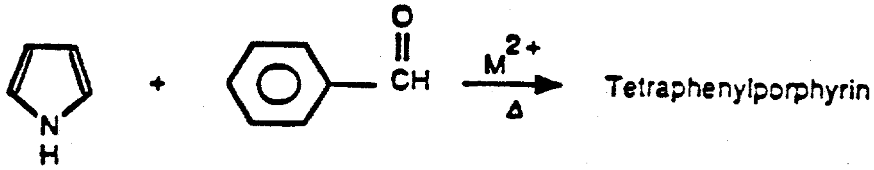
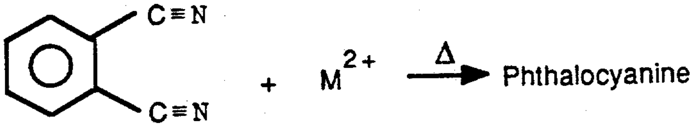
Alternatively, the cocondensation of pyrrole with benzaldehyde gives tetraphenylporphyrin [equation (5)].[30]



(5)

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



(6)

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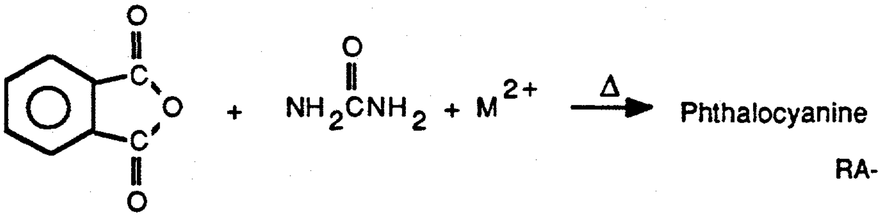
Alternatively, the condensation of phthalic anhydride and urea produces phthalocyanine [equation (7)].[31]



(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 7, we followed up on our earlier observation that PdTSPC/MgO oxidized methane to ethane at unprecedently low temperatures (375°C) by synthesizing two analogues of the PdTSPC and supporting these complexes on magnesia. NiTSPC on MgO produced only carbon dioxide, while with the palladium analogue PdTCPC (TCPC is tetracarboxyphthalocyanine) we did not observe methane oxidation. We had also reexamined the catalytic activity of several of the supported ruthenium clusters as a test of the catalysts' stability in storage over time. We found that apparently both activity and selectivity of these catalysts had declined over time. In this reporting period, we discovered that our catalytic flow reactor system had developed severe leaks which obviated the results of these tests. These leaks were identified and eliminated. We then ran a series of calibrations using a standard mixture of gases through the empty reactor at three temperatures: room temperature, 550°C, and 750°C. At 750°C, we observed several new peaks in the chromatogram which we attribute to cracking of higher hydrocarbons such as butane. This means that secondary reactions will lower the yields of such products in the dehydrocoupling of methane.

As part of our work under Task 1, we supported two of the ruthenium clusters ($H_4Ru_4(CO)_{12}$ and $H_2Ru_6(CO)_{18}$) on carbon. The purpose of doing this was to isolate the catalytic activity of the cluster from that of the support, since carbon has neither the acidity of zeolites nor the basicity of magnesia. We also used IR spectroscopy to investigate the origin of the different reactivities for $FeRu_3$ and Ru_4 supported on magnesia. We found that the mixed metal cluster decarbonylated at much lower temperatures than the pure ruthenium cluster under nitrogen. This decarbonylation occurs at much lower temperatures than the onset of activity for methane reforming. It does parallel the greater activity of the mixed metal cluster at lower temperatures. We also examined the Ru_4 cluster under methane/argon and found no significant differences in behavior in the carbonyl region when compared to the spectra under nitrogen.

We continued synthesizing analogues of PdTSPC/MgO for use as catalysts in the partial oxidation of methane. We had previously synthesized the NiTSPC/MgO system; in this period, we synthesized the platinum analogue. We also prepared a Pd exchanged zeolite, so that we could synthesize the phthalocyanine in a different environment and thus investigate the effect of the support on the reactivity of the complex. Synthesis of fluorinated analogues of some phthalocyanines and porphyrin species that had previously been investigated for activity in the partial oxidation of methane were attempted.

Task 1: Synthesis of Methane Reforming Catalysts

We synthesized two new types of supported ruthenium clusters during this reporting period. In these cases, we reacted $H_4Ru_4(CO)_{12}$ and $H_2Ru_6(CO)_{18}$ with the triethyl aluminum, then with carbon. We have two types of carbon available. One is a carbon molecular sieve obtained from Calgon Corporation. The pore openings in this material are in the range of 1-6 angstroms in diameter, so that molecules which can diffuse into the zeolite 5A pores should also "fit" into this carbon molecular sieve. Thus, we would expect the tetraruthenium clusters to be distributed on both the inside and outside of the carbon particles, whereas the hexaruthenium particles would be found only on the external surface area of the carbon molecular sieves. The second type of carbon available is Mogul L, available from Cabot Corporation, which is an acidic carbon black. This carbon black should correspond to alumina, with its lack of pore structure and heterogeneous distribution of acid sites.

We reacted both ruthenium clusters with the molecular sieve carbon. With the tetraruthenium cluster, we measured 0.5 equivalents of ethane per ruthenium cluster given off during the deposition reaction. This suggests that there may not be enough surface hydroxyl groups in the molecular sieve carbon accessible to the cluster for the hydrolysis reaction leading to surface attachment. This is not surprising, since the carbon molecular sieves are extremely inert, and we want to use the carbon as a support because of its inertness. The reactivity of both acidic and basic supports such as alumina or magnesia is related to the presence of surface hydroxyls. The other type of carbon we have available, Mogul L, is an acidic carbon black. The acidity of this substance is not nearly as great as a solid such as alumina. The acidic surface groups on this carbon can be hydroxyls, phenols, or carboxylic acids. All of these groups can react with the aluminum-carbon bond in our clusters to provide the surface attachment. The carbon black is a more suitable surface to use for these attachments because of this higher density of surface groups than found in carbon molecular sieves.

We had previously reported that $FeRu_3/MgO$ dehydrogenates methane at lower temperatures than the tetraruthenium cluster on the same support. At 750°C, the mixed metal cluster is ten times as active ($41.5\%_v$ methane conversion by the $FeRu_3$ cluster and $4.0\%_v$ methane conversion by the Ru_4 cluster). We have therefore investigated the behavior of these two systems under flow-through conditions by infrared spectroscopy using a diffuse reflectance (DRIFT) cell which can be heated to operating temperatures as a means of determining the source of the increased activity of the mixed metal system. In this reporting period, we have examined both magnesia supported clusters under nitrogen as well as Ru_4/MgO under methane. Examining the behavior of the clusters under nitrogen gives us a reference spectrum which we can subtract from the spectra obtained under methane. This subtraction, along with data workup using the Kubelka-Munk technique, gives us a difference spectra in which we can focus on changes due to reaction with methane.

Under nitrogen, we observed large differences in the spectra of these two clusters on magnesia at room temperature (Figure 2). The spectra we obtained for the Ru_4 cluster on magnesia is very similar to that obtained by Gates with $H_4Ru_4(CO)_{12}$ adsorbed onto magnesia and treated with helium at 100°C;[32] two broad peaks of equal intensity at about 2038 and 1965 cm^{-1}. Starting with $Ru_3(CO)_{12}$ and MgO, Guglielminotti has obtained the same spectra.[33] On alumina, an additional small peak is observed at about 2000 cm^{-1}.[34] The close resemblance of these four spectra is somewhat surprising. Gates has proposed that $H_4Ru_4(CO)_{12}$ reacts with the basic magnesia surface by deprotonation to give the anion $[H_3Ru_4(CO)_{12}]^-$ and hydrogen.[32] In our case, we observed the aluminum-carbon bond of the diethylaluminum unit reacting with the surface and attaching the cluster with release of ethane. We would expect this reaction to occur more readily than the deprotonation; however, with our current procedure, we are unable to observe any hydrogen release since it is a non-condensable gas. Hydrolysis of the aluminum-carbon bond is expected to immobilize the cluster through an oxygen-aluminum bond. Deprotonation should give a much more mobile surface cluster, since the bonding is ionic. The similarity of the spectrum suggests that rearrangement of the various starting clusters has occurred to give similar surface species. As an example, such rearrangement under mild conditions has been observed for $Ru_3(CO)_{12}$ on magnesia surfaces; a molecule of carbon dioxide is released, and the cluster $[HRu_3(CO)_{11}]^-$ is formed on the surface.[35]

The spectrum of the mixed metal cluster in Figure 1 is more complex. At least three peaks are observed at 2035, 2005, and 1975 cm^{-1}. This spectrum is similar to that obtained by Basset and Shore on reacting $H_2FeRu_3(CO)_{13}$ with hydrated magnesia;[36] our spectrum has a more intense peak at 1975 cm^{-1}. In both cases the peak due to a bridging carbonyl at ca. 1820 cm^{-1} is not observed. $Fe_2Ru(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ on alumina also give spectra identical to each other.[37] Basset[36] has shown that the major species on the magnesia surface is the anion $[HFeRu_3(CO)_{13}]^-$ by extraction with PPN^+Cl^- in dichloromethane. This identity is especially surprising since our elemental analysis of the metals on the surface show a large excess of iron; some of this may be due to iron

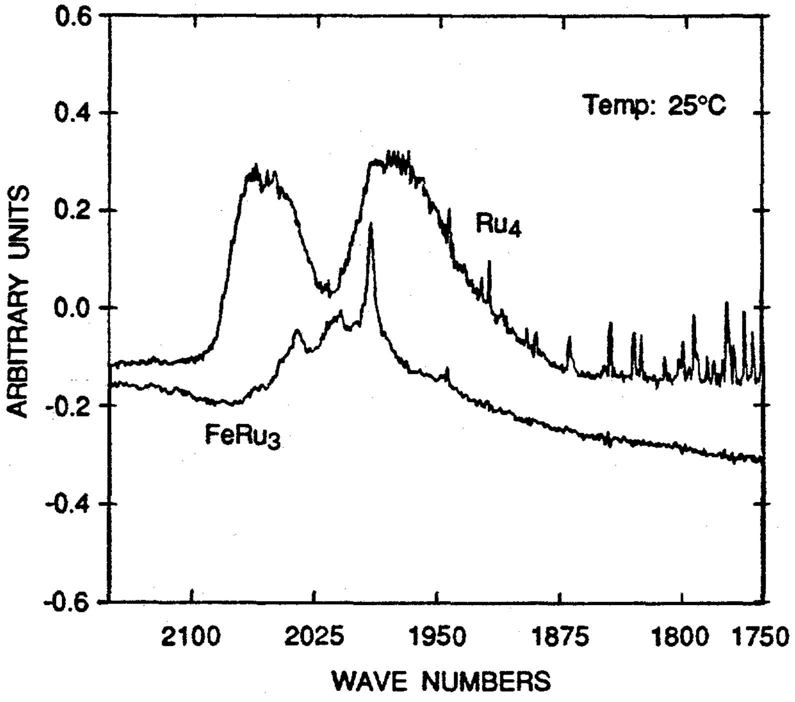

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Figure 2. Comparison of Ru_4 and $FeRu_3$ clusters on MgO under N_2.

impurities in the magnesia. Both our triethyl aluminum treated clusters therefore give the same spectrum as deprotonated clusters.

As these clusters are heated under nitrogen, the spectrum of $FeRu_3$/MgO changes over 100°C. At 200°C, a broad featureless peak is observed centered at ca. 1980 cm^{-1} (Figure 3). By 300°C, this feature is barely observable (Figure 4). Basset[36] found that the $[HFeRu_3(CO)_{13}]^-$ cluster on magnesia produced several moles of hydrogen per cluster when heated over 100°C. The origin of this hydrogen was proposed to be the water gas shift reaction between carbon monoxide and surface water. The final product was small metal particles. On alumina, decomposition of samples prepared with $Fe_2Ru(CO)_{12}$ first produced $Fe(CO)_5$, and then $Ru_3(CO)_{12}$.[38] The presence of iron accelerates the decomposition of the ruthenium cluster when they are absorbed together.[39] In our case, the source of water for the water gas shift reaction is more problematical. The magnesia we have used is heated to 450-500°C under flowing nitrogen, then taken into the dri-box after cooling. The solvents used in the deposition reactions were all dried before use. For the IR studies, the sample was loaded into the cell in the dri-box and sealed until nitrogen was purged through the cell.

The Ru_4/MgO catalyst, in contrast, is unchanged at 200°C. At 300°C (Figure 4), the intensity of the upfield peak has begun to decline. Both peaks have also shifted ca. 10 wavenumbers to a longer wavelength. At 400°C, the higher wavenumber band has disappeared (Figure 5). The other peak has declined in intensity and shifted to about 1905 cm^{-1}. Further heating of the sample caused this peak to continue and decline in intensity and shift to lower wavenumbers. By 600°C, only a very broad weak peak is observed at ca. 1880 cm^{-1}. This behavior is similar to that observed by Guglielminotti with a sample of ruthenium metal prepared from $Ru_3(CO)_{12}$ and magnesium hydroxide.[33] In this case, the shift in the peak arises from an annealing process. The results from these studies under nitrogen show that the mixed metal cluster decomposes at lower temperatures; this parallels the greater activity of this system in the methane dehydrocoupling reaction. The greater activity of the mixed metal system may be due to the presence of iron influencing the morphology of the ruthenium metal clusters formed.

We then examined the behavior of the Ru_4/MgO catalyst under methane. We used a $5\%_v$ methane/argon mixture as the source of methane in these experiments. A comparison of the two spectra in the carbonyl region under nitrogen and methane is shown in Figure 6. Both the relative peak positions and intensities are identical. Heating the Ru_4/MgO under methane produced the same behavior in this region as that described above under nitrogen. This can be seen in Figure 4, which compares the spectra obtained at 400°C. In both cases

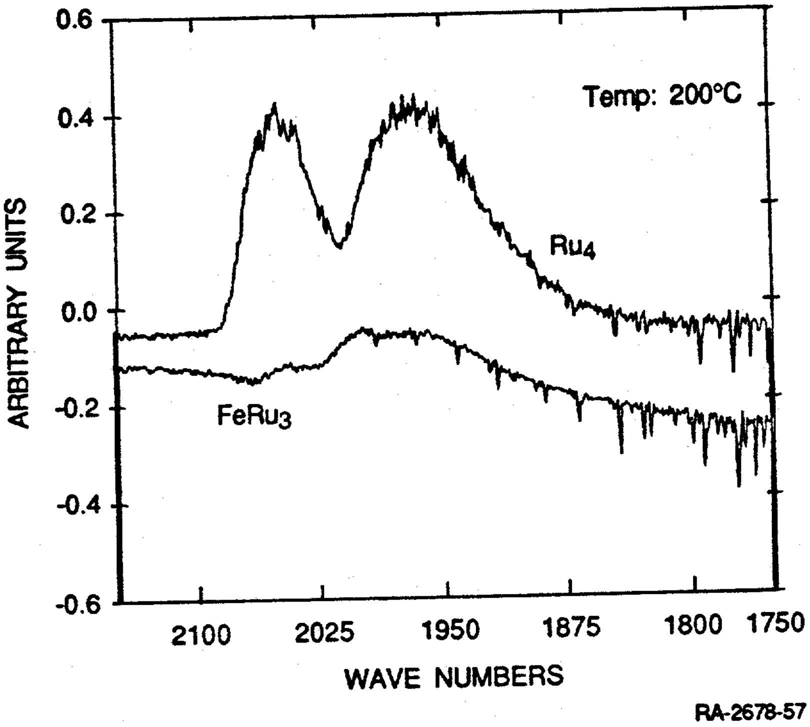

Figure 3. Comparison of Ru_4 and $FeRu_3$ clusters on MgO under N_2.

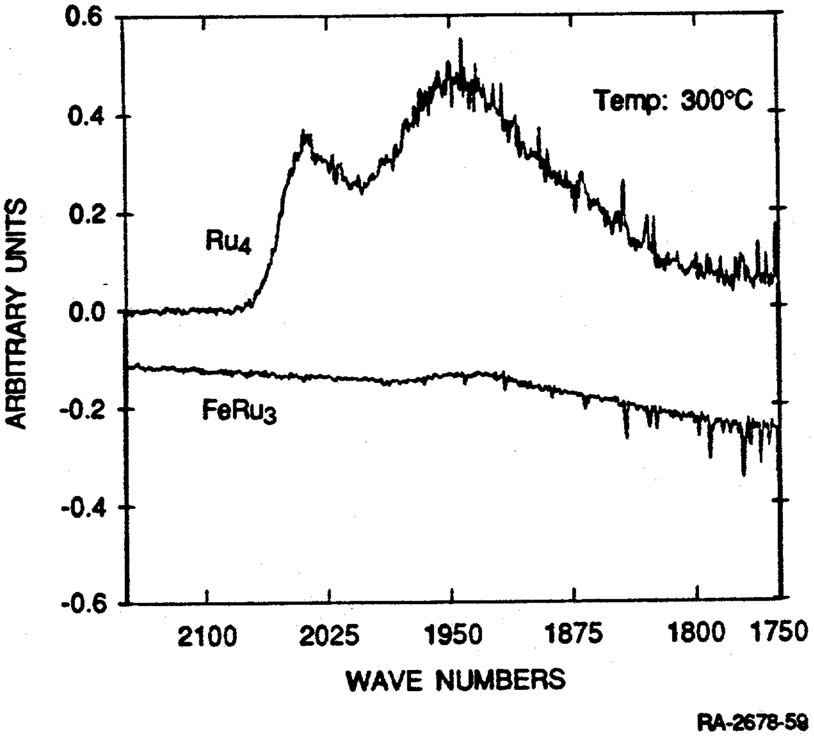

Figure 4. Comparison of Ru_4 and $FeRu_3$ clusters on MgO under N_2.

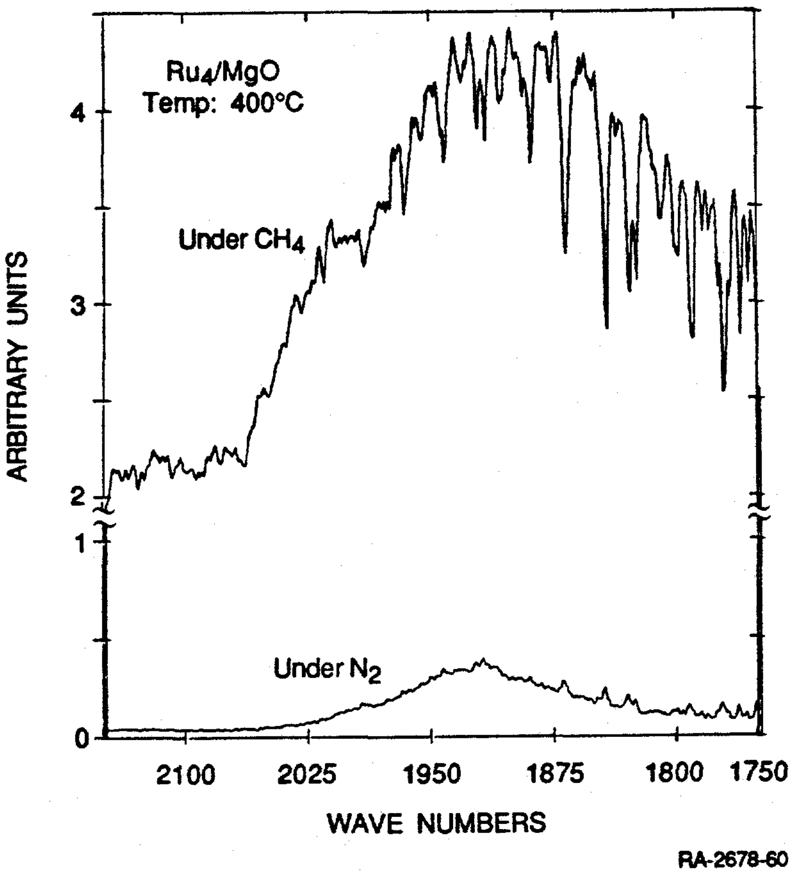

Figure 5. Comparison of Ru$_4$ cluster on MgO under CH$_4$ and N$_2$.

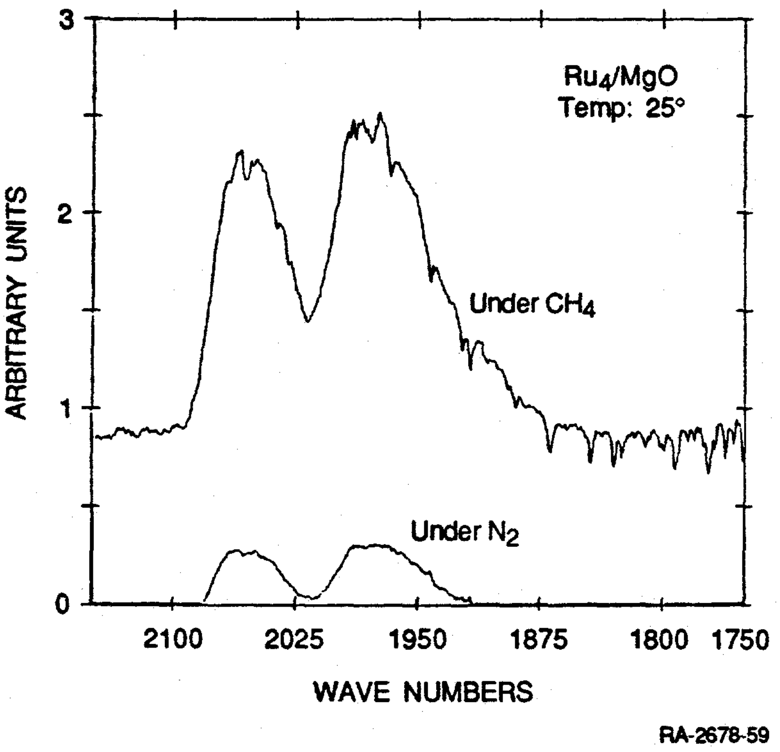

Figure 6. Comparison of Ru_4 cluster on MgO under CH_4 and N_2.

a slight shoulder is observed at about 2000 cm^{-1}, while the major peak is very broadly centered at 1935 cm^{-1}. Examination of the spectra in the C-H region shows that under methane the adsorbance of methane was greater for the MgO blank at room temperature. Two bands are observed at 2920 and 2850 cm^{-1}. These peaks did not change in relative position or intensity until over 600°C, when they were no longer observed. Under more reducing conditions (CO/H_2 at 275°C), Gates observed that $H_4Ru_4(CO)_{12}$ on magnesia was converted into $[Ru_6C(CO)_{16}]^{-2}$.[32] These results suggest that the methane is not reacting with our sample of Ru_4/MgO in the DRIFT cell. This may be due to the fact that in the conditions under which we obtained these spectra (5%$_v$ methane in the gas under relatively low pressures) the methane is relatively less concentrated than in our flow reactor (20%$_v$ methane and 150 psi). Use of a more concentrated methane gas stream would increase the probability of observing reaction in the DRIFT cell.

Task 2: Testing of Methane Reforming Catalysts

In the previous technical report, we discussed our reexamination of several dehydrocoupling catalysts in order to check the stability of the catalysts over long periods of storage. The results were very different from what we expected, which prompted us to reevaluate our catalytic flow reactor system. We discovered some major leaks in the system. Once this was uncovered, we removed the faulty parts and rebuilt the reactor system.

Once the reactor system was reconstructed, we ran a series of calibrations using a standard mixture of gases through the empty reactor at three temperatures: room temperature, 550°C, and 750°c. The mixture contained, in addition to C_1-C_4 saturated hydrocarbons, ethylene, hydrogen, carbon monoxide, carbon dioxide, oxygen, and nitrogen. This mixture was used to establish the relative response factors of these gases with respect to nitrogen, and how temperature affects these response factors in the empty reactor. Nitrogen is assumed to be inert under the reaction conditions, so that the volume percent of nitrogen remains constant under all conditions. Use of nitrogen as an internal standard enables us to minimize the effects of variations in sample volume on the measurement of our reaction products as the temperature is changed. This occurs since we know the volume percent of nitrogen, and the response factors of the hydrocarbons and hydrogen to nitrogen. In our calculations, we have assumed that the gases obey the ideal gas law, so that volume percent is directly proportional to mole percent. We have also assumed that the number of moles of gas exiting the reactor is equivalent to the number entering. At low conversions of methane, this assumption is justified because the change is small compared to the total number of moles of gas. Methane is about 20%$_v$ of the entering gas mixture. Even if 5%$_v$ of the methane reacts to give no gaseous products (an unlikely event), this means that the number of moles of gas leaving has changed only 1%, which is within the error limits of the GC.

When we raised the temperature of the empty reactor, we observed several major changes in our standard mixture. At 550°C, all of the hydrocarbons remain constant with the exception of ethylene which declines slightly. This may be due to the presence of oxygen in the standard gas mixture used. At 750°C, we observed cracking of the hydrocarbons. Several new peaks were observed in the chromatogram, which were attributed to the presence of propylene and butenes. The total C_2-C_4 saturated hydrocarbons declined drastically (C_4, 97%$_v$; C_3, 88%$_v$; C_2, 37%$_v$ of the amount at room temperature reacted) while the amount of methane and hydrogen present rose. These blanks demonstrate that the reactor itself can catalyze the further reactions of the primary hydrocarbon products at high temperatures, so that we can not determine the relative response factors of all the components to nitrogen at elevated temperatures. It also suggests that the conversions and selectivities we calculate are lower limits to the actual values, since the reactor can catalyze the back reaction of potential products such as propane to give methane and hydrogen. The area of the nitrogen peak in these injections remained constant, which is a good indication that the size of our injection volume has remained constant.

These results are also important for work we have proposed with using higher hydrocarbons in the reactant gas mixture. Incorporating small amounts of hydrocarbons such as found in natural gas into the gas mixture would be more realistic in terms of situations where these catalysts would be most useful. The presence of the higher hydrocarbons would help activate the methane for dehydrocoupling by generating free radicals. The results above suggest that such activation might be difficult to detect since the higher hydrocarbons undergo cracking at these temperatures to produce methane.

We next tested our reactant gas mixture of 20.8%$_v$ methane and 20.5%$_v$ nitrogen (balance helium) in the empty reactor at typical reaction conditions (150 psia, 50 ml/min flow rate). Using the response factor for methane calculated previously at room temperature, and setting the amount of nitrogen present as 20.5%$_v$ under all conditions, the amount of methane observed at three temperatures were: room temperature, 20.74%$_v$; 550°C, 20.85%$_v$; 750°C, 20.69%$_v$. This variation of <1% is well within the experimental error of the GC (2% according to the vendor), so that the use of room temperature response factors at higher temperatures does not introduce greater error into our calculations.

At the end of this reporting period, Dr. Wilson presented a paper describing our work on dehydrogenation catalysts during the methane activation symposium at the ACS meeting in Los Angeles. The paper was favorably received, and several suggestions for further experiments were received. Among the most interesting of these was a suggestion by Professor Lunsford to observe the intermediates in the production of the higher hydrocarbons. He suggested that once these hydrocarbons are being produced at a steady rate, the reactant gas should be switched to hydrogen and the carbon products desorbing 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. We intend to carry out such an experiment in the near future.

Task 3: Synthesis of Catalysts for Partial Oxidation of Methane

We synthesized analogues of PdTSPC in this reporting period, since the production of ethane by this species on magnesia is unprecedented at the low temperatures of our reaction. We successfully synthesized the platinum analogue of PdTSPC, using $PtCl_2$ as the metal salt by Busch's method.[40] This completes the series of three metals (nickel, palladium, and platinum) in the same family which have been substituted into the TSPC ligand. This will enable use to determine the effect of the metal when these complexes are supported on magnesia and used as partial oxidation catalysts. We have also prepared a palladium ion exchanged zeolite (Y type), which we plan to use for synthesizing PdTSPC in the pores of the zeolite. This would provide information on the effect of the support in the partial oxidations catalyzed by PdTSPC/MgO.

We attempted to synthesize perfluorinated (PF) analogues of some phthalocyanine (PC) and tetraphenylporphyrin (TPP) complexes encapsulated within the zeolite Y pores. These species are of interest due to their greater stability under oxidizing conditions.[41] We attempted to synthesize RuPFPC using a ruthenium exchanged zeolite Y as the source of the metal salt. RuPC was the most active species for methane oxidation in our earlier experiments. The material we produced did not show the expected PC chromophore; in particular, the band at 770 nm diagnostic of PC complexes was absent. Comparison to a sample of CuPFPC also revealed some differences. We are currently working on identifying this species. We were also unsuccessful in synthesizing an encapsulated PFTPP species using the procedure of Longo et al.[42] Further attempts at synthesizing perfluorinated species will be made in the near future.

Task 4: Testing of Methane Oxidation Catalysts

Dr. Chan presented a paper on our methane oxidation results in the methane activation symposium held during the recent meeting of the American Chemical Society. The questions asked centered on whether we had been able to observe the Ru=O species we have postulated as the active oxidant in the RuPC/Y system. This is a general question on the use of homogeneous catalysts that have been heterogenized: How might their reactivity change? Can it be established that the same active species are formed? This is an important study that would involve considerable in-situ monitoring of catalysts which we would like to pursue but is outside our current scope of work.

FUTURE WORK

The study we have carried out during this reporting period on examining the behavior of the tetrameric clusters $FeRu_3$ and Ru_4 on magnesia have shown that the mixed metal cluster decarbonylates much more readily under nitrogen. The Ru_4 cluster under both nitrogen and methane displays identical behavior. We need to examine the behavior of the $FeRu_3$ cluster under methane and compare it to both Ru_4/MgO under methane and $FeRu_3/MgO$ under nitrogen. Obtaining the spectra of other ruthenium clusters and mixed metal clusters (such as Ru_6 or $CoRu_3$) on magnesia under methane 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.[32] We will also attempt to reexamine the tetraruthenium and iron triruthenium clusters on magnesia under methane in order to observe any changes due to reaction with the methane.

Mixed metal clusters with tetranuclear metal cores are of interest, since we can study the effect of the metal composition and the starting cluster geometry on the systems' methane dehydrocoupling activity. We have already shown that the mixed metal $FeRu_3$ cluster is more active for methane dehydrocoupling than the corresponding Ru_4 complex. 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.[43-46] We intend to support the most interesting of these clusters on carbon (Mogul L first, then molecular 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 dehydrocoupling 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 can carry out Professor Lunsford's suggested experiment 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.

For the partial oxidation of methane, our efforts will be directed toward synthesizing analogues of the PdTSPC/MgO system that produces ethane. We have already begun this work by varying the metal or the substituent on the phthalocyanine ring

(NiTSPC or PdTCPC). The PtTSPC we have recently synthesized will be supported on magnesia and studied in the catalytic flow reactor. We will also reexamine the NiTSPC and PdTCPC systems after calibrating the GC and studying the effect of heating on a standard mixture of gases as we reported above for the methane dehydrocoupling reaction. The effect of the support on PdTSPC catalysts will also be studied by changing the support to zeolite Y or carbon. We would also like to compare the activity of another hydrocarbon activation catalyst, $(VO)_2P_2O_7$, to that of our phthalocyanine and porphyrin system. This vanadyl pyrophosphate is an industrial catalyst for the oxidation of butane to maleic anhydride.[47]

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. S. Uchiyama and B.C. Gates, J. Cat. (1988) 110, 388.
33. E. Guglielminotti, Langmuir (1986) 2, 812.
34. V.L. Kuznetsov, A.T. Bell, and Y.I. Yermakov, J. Cat. (1980) 65, 374.
35. L. D'Ornelas, A. Theolier, A. Choplin, J.-M. Basset, Inorg. Chem. (1988) 27, 1261.
36. A. Choplin, L. Huang, J.-M. Basset, R. Mathieu, U. Siriwardane, and S.G. Shore, Organometallics (1986) 5, 1547.
37. I. Boszormenyi, S. Dobos, L. Guczi, L. Marko, W.M. Reiff, Z. Schay, L. Takacs, A. Vizi-Orosz, Proceedings 8th Int. Cong. Catal., Vol. 5, Verlag Chemie, Weinheim, 1984, p. 183.
38. L. Guczi in Metal Clusters in Catalysis, Vol 29, ed. B.C. Gates, L. Guczi, H. Knozinger, Elsevier, Amsterdam, 1986, p. 553.
39. L. Guczi, Z. Schay, K. Lazar, A. Vizi, and L. Marko, Skurface Sci., (1981) 106, 516.
40. J. H. Weber and D.H. Busch, Inorganic Chemistry (1965) 4, 469.
41. P.S. Traylor, D. Dolphin, and T.G. Traylor J. Chem. Soc. Chem. Comm. (1984) p. 279.

42. F.R. Longo, M.G. Finarielli, and J.B. Kim. J. Heterocyclic Chem (1966) 6, p. 927.

43. G.L. Geoffroy and W.L. Gladfelter, J. Am. Chem. Soc. 99, 7565, (1977).

44. P.C. Steinhardt, W.L. Gladfelter, A.D. Harley, J. R. Fox, and G. L. Geoffroy, Inorg. Chem. 19, 332, (1980).

45. W.L. Gladfelter, G.L. Geoffroy, and J.C. Calabrese, Inorg. Chem. 19, 2569, (1980).

46. A.A. Bhattacharyya, C.C. Nagel, and S.G. Shore, Organometallics 2, 1187, (1983).

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