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CATALYTIC CONVERSION OF LIGHT ALKANES

Progress Report for the Period of July 1, - September 30, 1992

BY:

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Morgantown, West Virginia 26507

BY:

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MASTER

QUARTERLY PROGRESS REPORT

JULY 1, 1992 - SEPTEMBER 30, 1992

CATALYTIC CONVERSION OF LIGHT ALKANES

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SUN COMPANY

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ABSTRACT

The third and last quarterly report of 1992 on the Catalytic conversion of Light Alkanes reviews the work done between July,1992 and September 30, 1992 on the Cooperative Agreement. The mission of this work is to devise a new catalyst which can be used in a simple economic process to convert the light alkanes in natural gas to oxygenate products which can either be used as clean-burning, high octane liquid fuels, as fuel components or as precursors to liquid hydrocarbon transportation fuel.

During the past quarter we have continued to design, prepare, characterize and test novel catalysts for the mild selective reaction of light hydrocarbons with air or oxygen to produce alcohols directly. These catalysts are designed to form active metal oxo (MO) species and to be uniquely active for the homolytic cleavage of the carbon-hydrogen bonds in light alkanes producing intermediates which can form alcohols. We continue to investigate three molecular environments for the active catalytic species that we are trying to generate: electron-deficient macrocycles (PHASE I), polyoxometallates (PHASE II) and framework-substituted zeolites (PHASE III).

PHASE I - Major advances have been made in this area during the past quarter. We have demonstrated for the first time that a simple porphinic macrocyclic iron complex having only [redacted] substituents in the meso-position is an active catalyst for light alkane oxidation. The importance of this finding is threefold. First, the catalyst can be made by a simple [redacted] [redacted] Secondly, the first demonstration of activation of the macrocycle by meso-substitution with a group other than perfluorophenyl both substantiates the theory on which this line of research is predicated and opens the door to the use of a variety of potentially more electron

deficient substituents. Finally, use of the electron withdrawing [redacted] instead of the heavy and costly perfluorophenyl group greatly lessens catalyst cost while potentially enhancing per pound activity of the iron catalyst. This work is of particular importance preliminary to entering the proof-of-concept phase.

PHASE II - We have completed all of the planned work in this area listed in the SOW for the first three years of the Cooperative Agreement. Correlations have been found between metal reduction potential and catalytic activity but the magnitude of the effects have been small relative to those found on the PHASE I systems and have also been difficult to interpret. Because of the robustness of polyoxoanionic systems, some work will continue especially in the areas of activation of methane and ethane.

PHASE III - Work continues to show promise for methane and ethane oxidation to alcohols. New and more active zeolitic systems incorporating iron, cobalt and manganese have been synthesized and tested during the past quarter but, though active, were not as stable as the systems prepared and tested earlier this year. We can now catalytically activate methane below 365°C and anticipate generating even more active catalysts in the planned future research phase of the Cooperative Agreement.

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1.0 INTRODUCTION

We have found a family of new catalytic materials which, if successfully developed, will be effective in the conversion of light alkanes to alcohols or other oxygenates. Catalysts of this type have the potential to convert natural gas to clean-burning high octane liquid fuels directly without requiring the energy-intensive steam reforming step. In addition they also have the potential to upgrade light hydrocarbons found in natural gas to a variety of high value fuel and chemical products. In order for commerically useful processes to be developed, increases in catalytic life, reaction rate and selectivity are required. Recent progress in the experimental program geared to the further improvement of these catalysts is outlined in Sections 5 and 6.

2.0 PURPOSE

The mission of the work presented in this quarterly report is to generate novel catalytic technology which will permit the development of a simple, efficient and economical process for the direct conversion of natural gas to liquid transportation fuels. This process should be simple enough to liquify natural gas economically even at a remote reservoir site. It is a further mission of this work to find new routes from natural gas or its components to high value oxygenates by direct air-oxidation using these new catalysts.

The technical objective of the research is to design the first effective molecular catalyst for the direct air-oxidation of the hydrocarbons found in natural gas to an alcohol-rich oxidate which can either be used directly or converted into gasoline <u>via</u> known technology. The development of an efficient catalyst for the smooth and selective oxidation of light alkanes to alcohols will not only provide a solution to the problem of liquifying natural gas, but will create new opportunities to utilize the relatively inexpensive and abundant light alkanes for the production of a variety of valuable fuel and chemical products. Processes for converting natural gas or its components (methane, ethane, propane, and the butanes) to alcohols for use as motor fuels, fuel additives or fuel precursors will not only add a valuable alternative to crude oil but will produce a clean-burning, high octane alternative to conventional gasoline.

3.0 TECHNICAL BACKGROUND

The First Quarterly Report of 1992 for Catalytic Conversion of Light Alkanes Cooperative Agreement, Section 3.0, can be consulted for details of the technical background relating to this project.

4.0 METHODOLOGY

Details of the suprabiotic methodology to be used to conduct research on the Catalytic Conversion of Light Alkanes can be found in Section 4.0 of the First Quarterly Report of the Cooperative Agreement.

5.0 RESULTS AND DISCUSION

The three major thrusts of the research program are catalysis by A) metals in electron deficient macrocycles (PHASE I), B) Polyoxometallates (PHASE II), and C) metals in regular oxidic matrices (PHASE III).

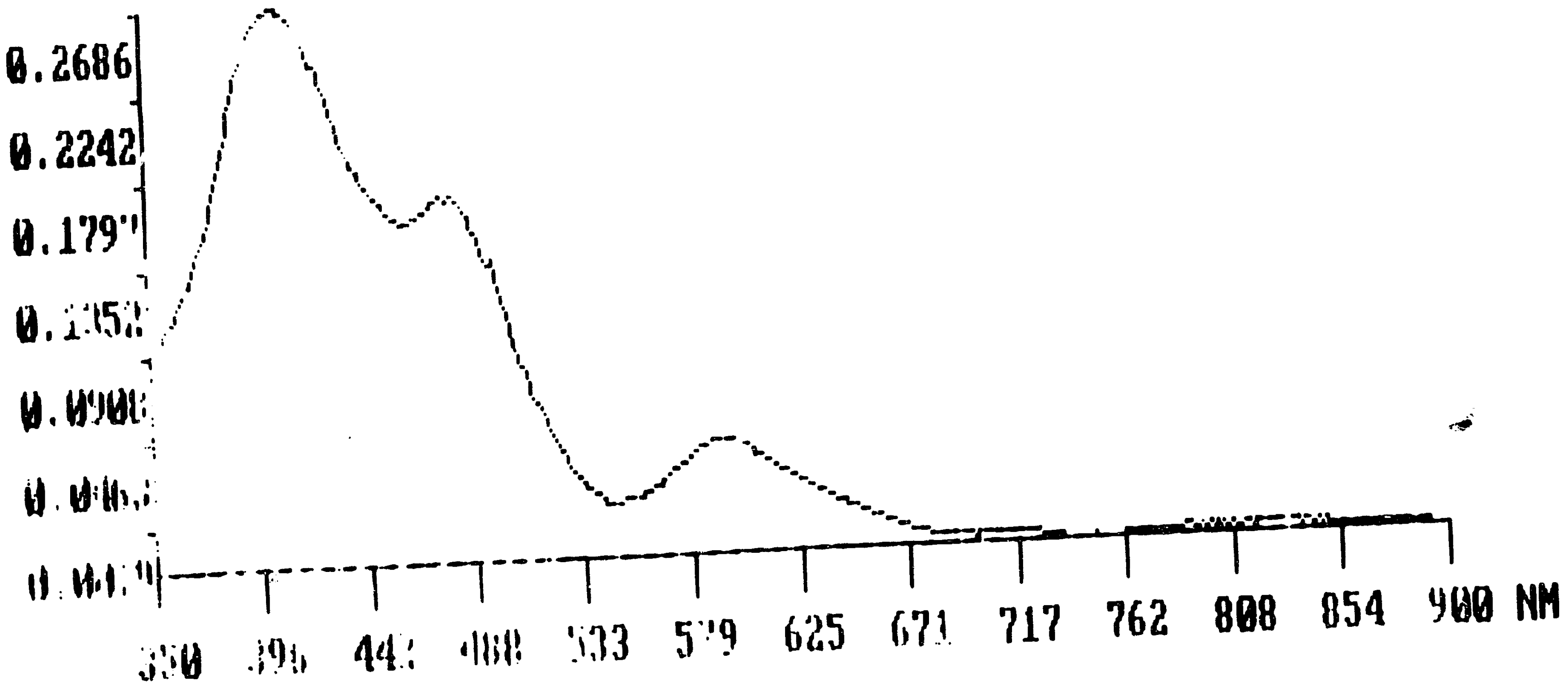


FIGURE 5-1

REPORTED ABSORPTION SPECTRUM OF Fe($TPPF_{20}\beta$-Cl_8)Cl

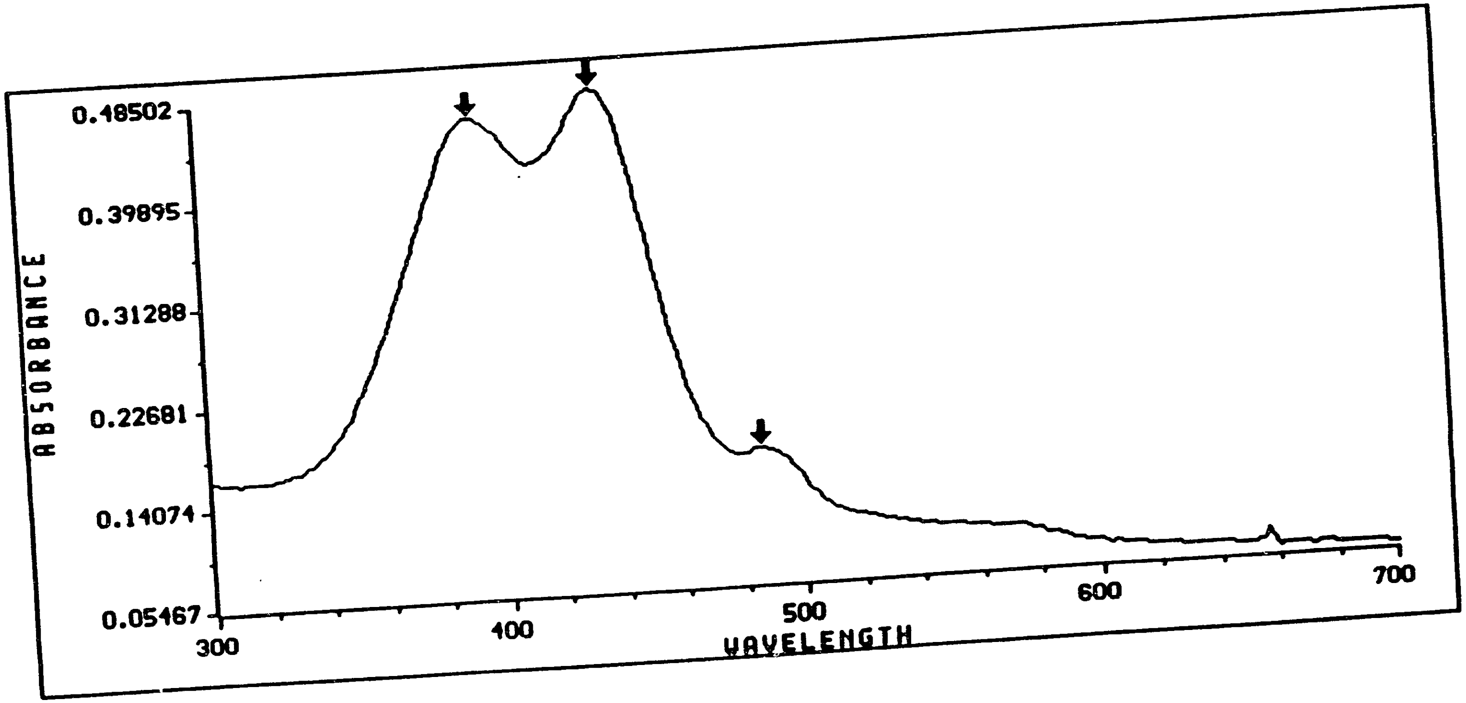
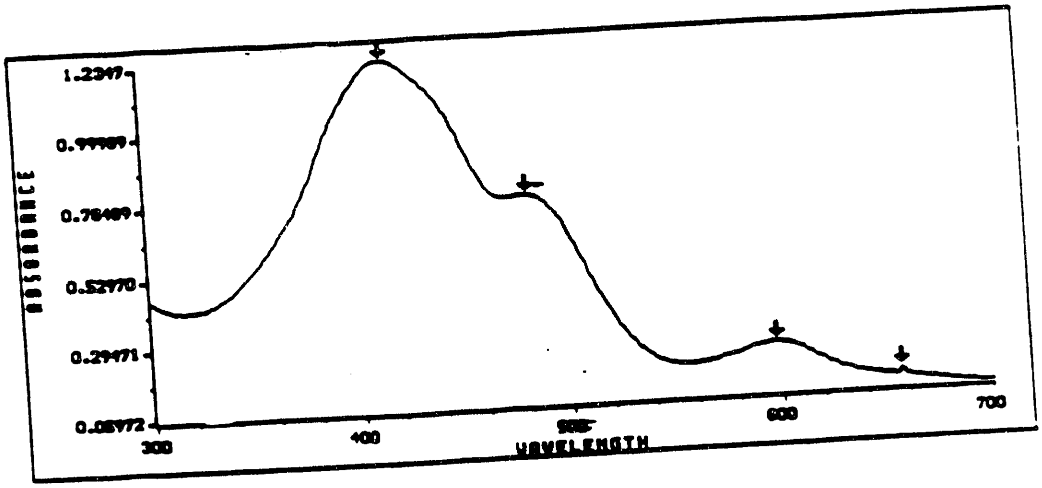


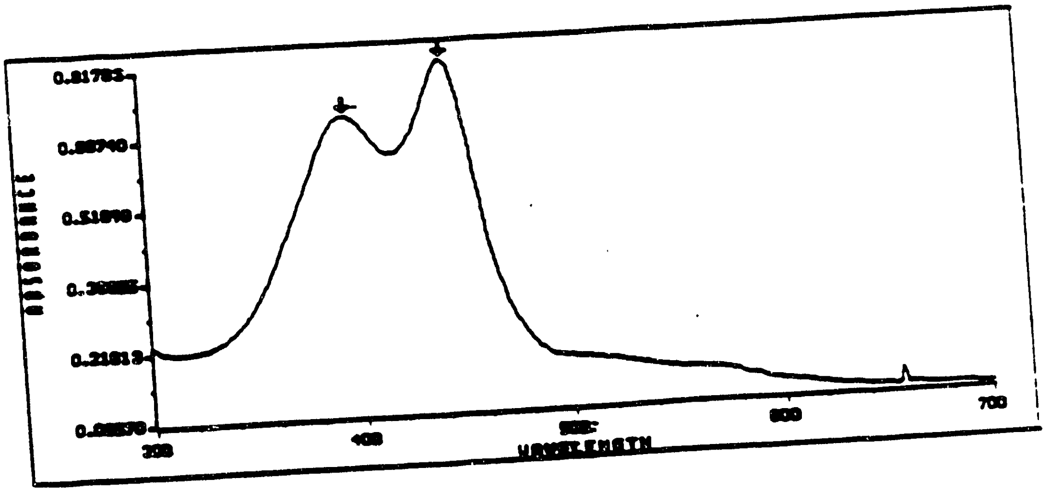
FIGURE 5-2

ABSORPTION SPECTRUM OF HCl-TREATED PRODUCT

(LARGELY Fe(TPPF$_{20}$-βCl$_8$)Cl) the sample or may have been produced by demetallation. This spectral change after chromatography and after acid treatment was also observed with Fe(TPPCl$_{28}$)Cl (Figure 5-3). The identification of the axial ligand of porphinatoiron(III) complexes is important due to the observation that the chloro species shows an induction period during catalysis.



A: After Chromatography; λ_{max} 416, 482, 598nm



B: After HCl Treatment ; λ_{max} 396, 444nm

FIGURE 5-3

EFFECTS OF CHROMATOGRAPHY (MEOH)
AND HCl TREATMENTS ON AN
Fe(TPPF$_{20}\beta$-Cl$_8$) COMPLEX

5.3.2. METHANE OXIDATIONS UNDER DIFFERENT CONDITIONS

In past reports we have stressed the critical nature of the methane oxidation conditions on methanol selectivity. We have shown how under the same conditions of temperature, pressure and flow rate, selectivities of the iron sodalite catalyzed oxidation of methane could vary from under 20% in a back mixed spinning basket reactor to under 30% in a fully packed down-flow reactor to around 50% in a top-loaded down-flow reactor to 70% in a flow reactor aided by product removal by reactive distillation. Table 5-4 shows how changes in feed mixture, catalyst loading and flow rate in yet another reactor design described below can also affect product selectivity. A combination of higher flow rate, higher oxygen partial pressure, different configuration and the presence of a glass frit all may contribute to poorer methanol selectivity.

5.3.2.1 Experimental Details of Methane Oxidations

Some recent experimentation in our laboratory was conducted under reactor test condiditons including relatively high proportions of air in the feed. These runs were conducted in a quartz-lined downflow packed bed reactor in which 2-4 ml of an 18/35 mesh solid catalyst were packed over a quartz frit. About 4 ml of empty space preceded the catalyst in the heated zone and abut 5 ml of empty space was present below the frit in the heated zone. A thermocouple was inserted into the middle of the packed bed in most runs, but this was removed in others to ensure no contribution by the thermocouple material to catalysis. Prior to the reactor, methane and air were mixed and preheated in a hastelloy C CSTR operated at an impeller speed of several thousand RPM and 300°C. All runs were conducted at 820+/-5 psig.

Control runs were conducted with silica gel packing in the reactor which was expected to provide surface for alkylperoxy radical quenching but not to contribute to catalysis beyond the homogeneous thermal reaction. Several batches of [Fe]SOD with and ithout further Fe2+ exchange were examined as well as MeAPO-type molecular sieves containing manganese, and a perfluorophthalocyanineiron(II) compound supported on either silica or [Fe]SOD. Data measured after 300-400 minutes on-stream are presented in Table 5-4. Each data point represents the mean of at least four gas analyses and three liquid analyses; additional data from these runs including 21 additional analyses for each run are archived at the Sun Laboratories. Since in all but one case, the catalysts had not been aged on-stream, these data represent minimum performance for the [Fe]SOD cases and perhaps also for the MnAPO catalysts.

Comparison of the present experimental results to lower oxygen content runs leads one to the general conclusion that methane conversion is not necessarily increased by a higher partial pressure of oxygen in the feed. Despite higher oxygen partial pressure, conversions of about 2-6% were observed in the present runs, on average, just as had been observed for 3:1 methane:air mixtures previously. Methanol selectivity was found to be generally lower than in earlier runs at higher methane concentration, however. Considering the strong tie between conversion and selectivity, i.e., at constant oxygen conversion, the more methanol produced relative to CO_2, the greater the conversion of methane, it is not surprising that methane conversion was not observed to be higher in our recent runs since modelling studies predict that CO_2 formation is increased at the expense of methanol by higher oxygen concentration.

Another area of continuing interest is formaldehyde production. Using a differential pulse polarographic analytical technique, we have examined the formaldehyde yield from a number of methane oxidation runs reported above and have found a correlation between yields of methanol and formaldehyde in most runs examined (Figure 5-13). This suggests that a common progenitor to methanol and formaldehyde might exist, in agreement with our homogeneous reaction kinetic model prediction. The formaldehyde yield was found to be roughly 10-15 times smaller than the methanol yield in our runs, also consistent with semiquantitative model predictions made earlier.

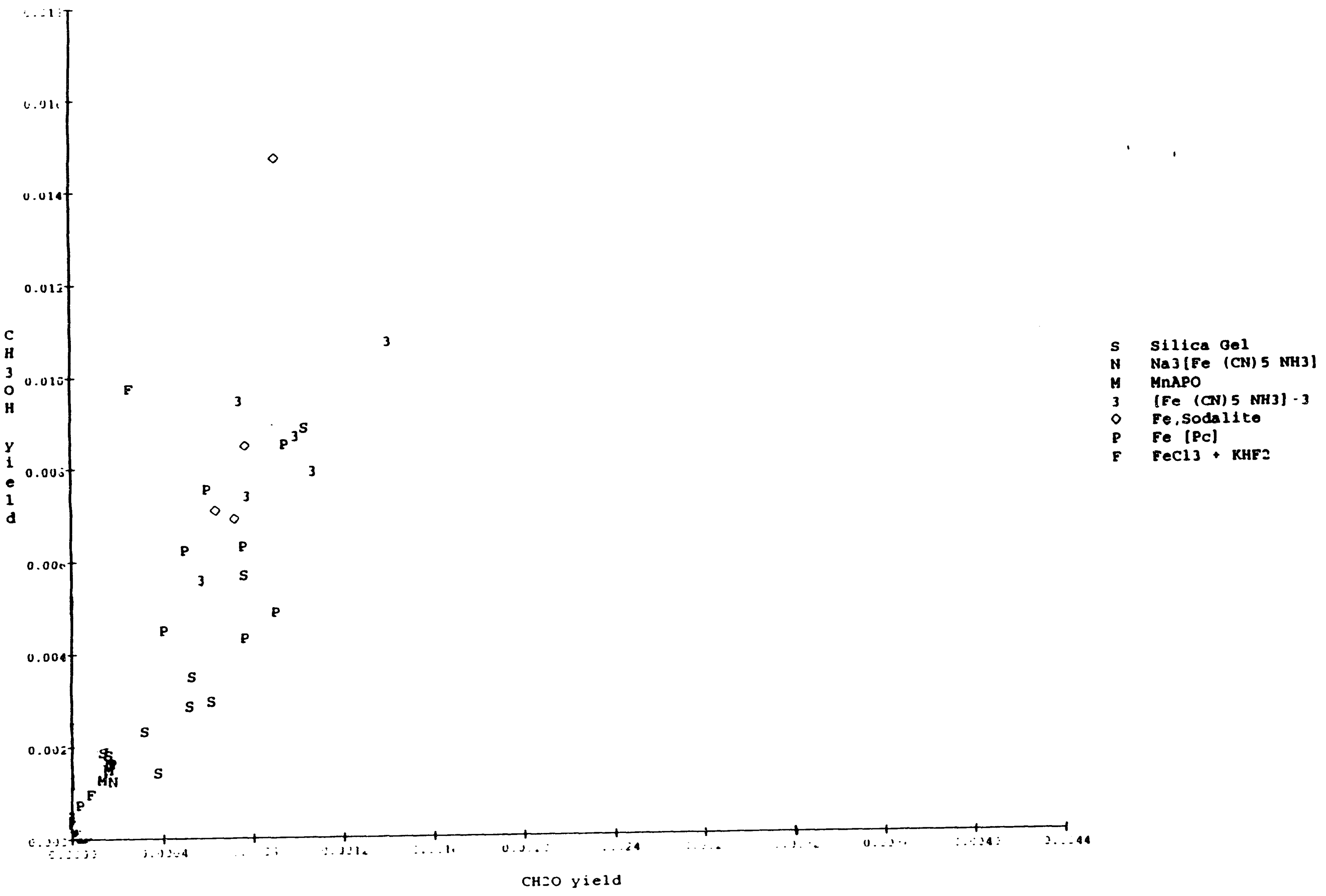
TABLE 5-4

OXIDATIONS OF METHANE AT HIGH O_2 AND GHSV[a]

CATALYST	MLS CAT	CH4/ AIR	GHSV (TOT. VOL.)	GHSV (CAT)	T°C	CH_4 CONV.,%	O_2 CONV.,%	CH_3OH SEL.,%
[Fe]SOD	1.3	2.23	2,724	14,668	414	5.7	93	16
	1.3	2.23	2,724	14,668	414	5.6	94	15
	2.7	2.23	2,724	7,063	405	4.8	79	22
	2.7	2.23	2,724	7,063	375	0.6	64	9
Fe^{2+}[Fe]SOD	3.3	2.23	2,724	5,779	408	6.8	99	20
MnAPO-5	5.0	2.23	2,724	3,814	380	4.9	96	3
Fe-FPc/[Fe]SOD	2.1	2.23	2,724	9,080	407	5.8	94	15
	2.1	2.23	2,724	9,080	407	5.4	96	15
Fe-FPc/SiO_2	3.1	2.23	2,724	6,151	406	3.4	72	22
	3.1	2.23	2,724	6,151	375	1.3	62	12
SiO_2gel	3.2	2.23	2,724	5,959	405	3.0	78	30
	3.2	2.23	2,724	5,959	380	2.1	22	0.4

[a] See experimental detail.

CH3OH yield vs. CH2O yield



Data:yield_grid Graph:yield_crt

6.0 CONCLUSIONS

We have completed all of the laboratory tasks set out in the SOW for the Cooperative Agreement. More importantly, we have found highly active catalyst systems which give unprecedented rates of activation of light alkanes to form oxygenates in liquid and vapor phase. Results of our research confirms many of our intial ideas and suggests that there is a high probability of success in achieving practical processes for alkane conversions based on the new science and technology which we have generated. Recent success in making potentially cheaper and more active catalysts is particularly important as we enter the proof-of-concept stage for a process to make tert-butyl alcohol from C_4 gas components. Continued research is likely to result in future process technology for C_1-C_3 gas components as well. Details of each phase of this research will be reported in Topical Reports in the near future. A final report will issue shortly.

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