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DIRECT CATALYTIC CONVERSION OF METHANE
AND LIGHT HYDROCARBON GASES

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CONTENTS

INTRODUCTION AND SUMMARY	1
TECHNICAL APPROACH	2
Task 1: Synthesis of Advanced Reforming Catalysts for Methane	2
Task 2: Testing of Methane Reforming Catalysts	3
Task 3: Synthesis of Oxidation Catalysts for Methane	4
Task 4: Testing of Methane Oxidation Catalysts	6
RESULTS AND DISCUSSION	7
Task 3: Synthesis of Oxidation Catalysts for Methane	8
Task 4: Testing of Methane Oxidation Catalysts	10
FUTURE WORK	13
EXPERIMENTAL DETAILS	15
Preparation of Tetrasulfophthalocyanine (TSPC) Complexes....	15
Preparation of Magnesium Oxide Supported TSPC Complexes ...	16
Testing of Methanol Decomposition	16
REFERENCES	17

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 gasifier² 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, we synthesized several phthalocyanine catalysts supported on magnesia (MgO) in Task 3. In Task 4 we have tested these catalysts for oxidation of methane and did a number of blank experiments to determine the cause of the low methanol yield we have observed.

Magnesia supported catalysts were prepared by first synthesizing the various metal tetrasulfophthalocyanines (TSPCs), converting them to the acid form, and then supporting these complexes on a basic support (MgO) by a neutralization reaction. The metals used were Ru, Pd, Cu, Fe, Co, Mn, and Mo. The metal loading was generally less than 0.5%, except for Mo. CoTSPC was also synthesized in zeolite Y using our standard template techniques described in Quarterly Report No. 1.

These complexes were examined for catalytic activity in the oxidation of methane. The PdTSPC/MgO had greater activity, and oxidized some of the methane (selectivity of 2.8% from the methane oxidized at 375°C) to ethane. This is a much lower temperature for this reaction than previously reported in the literature.

We also examined the reactivity of various components of the system in the oxidation of the product methanol. The reactor showed some activity for the oxidation of methanol to carbon dioxide. When zeolite or magnesia were added, this activity increased. The magnesia oxidized most of the methanol to carbon dioxide, while the zeolite reduced some of the methanol to hydrocarbons. With oxygen in the feed gas stream (i.e., the conditions of our methane oxidation), a very large fraction of the methanol was oxidized to carbon dioxide when passed over magnesia. From this, we can conclude that any methanol formed in the oxidation of methane would probably be destroyed very quickly on the catalyst bed.

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

*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)].

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, $Rh_2(2\text{-hydroxy-6-methylpyridine})$. Clusters are prepared from the hydridocarbonyl clusters by relying on reactions such as (2) and (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 pressure²⁸ (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.

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

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

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 AND DISCUSSION

In Quarterly Report Number 5, we reported the results of using magnesia supported ruthenium complexes as methane dehydrogenation catalysts. We observed that these novel systems were active at lower temperatures than the same complexes anchored to acidic supports such as zeolite Y or alumina. The distribution of hydrogen and hydrocarbon products from these reactions were also different on the basic magnesia from the other supports.

We synthesized the tetra-sulfophthalocyanine (TSPC) complexes of the following metals; Ru, Cu, Pd, Fe, Co, Mn, and Mo, and supported them on magnesia by using the magnesia to neutralize the acidic phthalocyanines. The cobalt species was also synthesized as an encapsulated complex in zeolite LZ-Y52. Elemental analysis of the catalysts showed that the amount of metal loading on the magnesia was generally less than on acidic supports such as alumina or zeolite.

The magnesia supported catalysts were tested for catalytic activity toward methane oxidation reactions. These reactions were carried out at 375-450°C. The complexes appeared to decompose at 450°C on magnesia under these reaction conditions. Low conversions of methane were observed for all the catalysts examined. The sole products observed for most metal complexes were carbon dioxide and water.

The PdTSPC/MgO system was the most active (1.4% conversion at 375°C, flow rate of 50 ml/minute). It also was the only one of these systems to yield products other than carbon dioxide and water, converting part of the methane to ethane. This reactivity is unprecedented in methane oxidation systems at such a low temperature. The selectivity to ethane was 2.8% at 375°C, and declined at higher temperatures as the activity increased.

Several blanks were run for the methane oxidation systems during this reporting period. It was found that the supports (MgO and zeolite)

alone would convert methanol to carbon dioxide and hydrocarbons under these reaction conditions. For zeolites, the selectivity to hydrocarbon was fairly good. These studies point out the need for supporting the organometallic complexes on a support which itself is inactive for methane oxidation.

Task 3: Synthesis of Oxidation Catalysts for Methane

All of the complexes synthesized during this reporting period are tetra-sulfophthalocyanines. These complexes were chosen so that the acidic sulfonic substituents on the phthalocyanine nucleus would enhance the binding of the metal complex to the basic magnesia support. The first step in the synthesis of the MgO anchored complexes is the synthesis of the individual metal TSPC complexes. These were prepared by the reaction of mono-sodium-4-sulfophthalic acid, urea, ammonium chloride, and metal salt in the presence of catalytic amounts of ammonium molybdate at 180°C. The metal compounds used were CoCl_2 , FeCl_2 , MnSO_4 , CuCl_2 , $\text{Ru}_3(\text{CO})_{12}$, and $\text{Mo}(\text{CO})_6$. The acid form of the complexes were obtained by treating these complexes with 2N HCl. These complexes were then dissolved in DMF and added to the MgO with stirring. After two hours, the reaction was filtered and the MgO powders washed with DMF and acetone, then dried overnight at 60°C in a vacuum oven.

The CoTSPC complex was successfully synthesized entrapped in zeolite Y. This was done by first ion-exchanging the cobalt ions into LZ-Y52 zeolite. The Co/Y was then suspended in N-methylpyrrolidinone (NMP); the sodium salt of 4-sulfophthalic acid was then added with urea and ammonium chloride to form the phthalocyanine around the cobalt ions in the zeolite. Ammonium molybdate was added in catalytic quantities. The reaction was refluxed for five hours, then cooled and filtered. The zeolite was washed with NMP, then acetone, and finally dried under vacuum at 60°C overnight. Success in this synthesis was indicated by the greenish-blue color of the zeolite, which is indicative of phthalocyanines. A similar reaction using Fe/Y as the metal template failed, most likely due to the prior oxidation of the Fe^{2+} to Fe_2O_3 .

The elemental analyses of five of these MgO supported complexes are displayed in Table 1. Assuming that all of the carbon present is associated with the phthalocyanine complex, the Ru and Cu complexes are the most completely metallated on the support. The Fe and Pd systems appear to have an small excess of unmetallated phthalocyanine present; this demetallation could have occurred in the acidification of the complex, since the complex was used directly after this step. The results for the MoTSPC/MgO system show that a large excess of molybdenum is associated with this system. This abnormally high metal content is most likely due to the presence of molybdenum carbonyl fragments in the MoTSPC used in the deposition reaction. If so, more oxidizing conditions during the acidification step should remove much of this excess molybdenum.

Table 1
ELEMENTAL ANALYSES OF MgO SUPPORTED CATALYSTS

	Experimental				Theoretical ^a			
	%C	%H	%N	%M	%C	%H	%N	%M
FeTSPCMgO	2.26	0.73	0.88	0.24	2.26	0.07	0.66	0.33
RuTSPCMgO	1.95	0.98	0.42	0.45	1.95	0.06	0.57	0.51
PdTSPCMgO	1.05	0.47	0.45	0.18	1.05	0.03	0.31	0.29
CuTSPCMgO	2.37	0.56	0.62	0.37	2.37	0.07	0.69	0.39
MoTSPCMgO	2.36	0.93	0.77	10.21	2.36	0.07	0.69	0.59

^aCalculated based on carbon content.

We have used these results to calculate the concentration of the metal complex per 100 g of magnesia. As shown in Table 2, the concentration for all the complexes except Pd are approximately 0.05 moles per 100 g MgO. The Pd loading is about half of this. This may be related to the observation that PdTSPC/MgO is the only complex that converts methane into higher hydrocarbons under the reaction conditions (see below).

Table 2

METAL LOADING AND COMPLEX LOADING OF THE
MAGNESIUM OXIDE SUPPORTED CATALYSTS

<u>Catalyst</u>	<u>Metal loading (Wt%)^a</u>	<u>Complex loading (mol/100g)^b</u>
FeTSPCMgO	0.24	0.052
RuTSPCMgO	0.45	0.047
PdTSPCMgO	0.18	0.026
CuTSPCMgO	0.37	0.054
MoTSPCMgO	10.21	0.057

^aFrom elemental analysis.

^bMoles of complex were calculated based on the carbon weight from the elemental analyses.

Task 4: Testing of Methane Oxidation Catalysts

We have tested the MTSPC/MgO systems for methane oxidation at temperatures from 375-450°C. Nitrogen was used as an internal standard and the 1.0:1.0:0.1 mixture of CH₄:N₂:O₂ was fed to the reactor at a rate of 50 mls/min. The results of these tests are presented in Table 3. The amount of methane conversion is very low in all cases. This table also contains the results of the blank reaction using MgO alone as the oxidation catalyst. Several of the metal complexes (Mn, Mo, Cu, Co and FeTSPC) had activity less than or equal to that of the magnesia without any metal loading. The two complexes more active than the blank were RuTSPC and PdTSPC. The Ru complex oxidized 1.3% of the methane to carbon dioxide at 375°C; the activity rose to 2.6% conversion at 450°C. At lower flow rates (10 ml/min) the conversion was higher (5.4% and 16.7% at 375 and 450°C, respectively). Carbon dioxide was the only carbon product observed in these reactions. We also tried CoTSPC on zeolite Y at 250-450°C, but observed no oxidation products.

Table 3

ACTIVITY OF MgO SUPPORTED METHANE OXIDATION CATALYSTS

Catalysts ^a	Temp. (°C)	%Conversion of Methane	%Selectivity ^b	
			CO ₂	C ₂ H ₆
PdTSPCMgO	375	1.4	97.2	2.8
	400	2.6	97.8	2.2
	450	5.7	99.7	0.3
FeTSPCMgO	375	0.8	100.0	0.0
	400	0.6	100.0	0.0
	450	1.5	100.0	0.0
RuTSPCMgO	375	1.3	100.0	0.0
	400	2.0	100.0	0.0
	450	2.6	100.0	0.0
CoTSPCMgO	375	0.6	100.0	0.0
	400	0.8	100.0	0.0
CuTSPCMgO	375	0.7	100.0	0.0
MnTSPCMgO	375	0.6	100.0	0.0
	400	0.5	100.0	0.0
MoTSPCMgO	375	0.8	100.0	0.0
	400	0.7	100.0	0.0
	450	0.9	100.0	0.0
MgO	375	0.8	100.0	0.0
	400	1.6	100.0	0.0
	450	1.9	100.0	0.0

^aCondition: Pressure = 1 atm, CH₄/O₂ = 10, GHSV = 5000 h⁻¹.

^bSelectivity was calculated based on carbon number.

The PdTSPC/MgO system was the most active of the MgO systems, converting 1.4% of the methane at 375°C and 5.7% at 450°C. Ethane as well as carbon dioxide was produced in these reactions; no methanol was observed. The selectivity for ethane was 2.8% at 375°C, declining to 0.3% at the higher end of the temperature range. This oxidative

coupling of methane to ethane is unprecedented at such low temperatures. Several literature examples of this reaction are collected in Table 4. Our PdTSPC/MgO system operates at much lower temperatures and as a result has lower methane conversions.

Table 4

LITERATURE EXAMPLES OF OXIDATIVE METHANE COUPLING CATALYSTS

Catalyst	CH ₄ /O ₂	Temp (°C)	CH ₄ Conversion (%)	Selectivity	
				C ₂ (%)	Ref.
LiMgO	2	720	37.8	50.3	32
Sm ₂ O ₃	6	750	6.5	60.0	33
BaTiO ₃	2	750	n.r. ^a	18.5	34
NaCl/MnO	2	750	32	48.9	35
Li ₂ O/BeO	2	760	37.7	65	36

^an.r. = not reported.

Our inability to observe methanol as a partial oxidation product was very puzzling, so we decide to study the reaction of methanol over these catalyst supports under our reaction conditions. Helium was used as the carrier gas, with or without oxygen present. The reactant gas mixture containing methanol was introduced into our reactor at 300 or 375°C. The results have been collected in Table 5. The reactor itself (first line) decomposes some MeOH at our typical reaction temperatures. Adding support materials such as zeolite Y or MgO increases this reactivity. Over MgO, most of the reacting methanol is converted to carbon dioxide or methane. A small amount of higher (C₂-C₄) hydrocarbons are also produced. Adding oxygen and passing the gas stream over MgO increases the reactivity so that most of the methanol is converted into carbon dioxide or methane; the selectivity to higher hydrocarbons does not change in total, although the selectivity to the individual carbon numbers changes slightly. In light of this observation,

it is therefore not very suprising that we have been unable to observe methanol in the oxidation reactions reported in Table 3. The observation of large amounts of C₂, C₃, and C₄ hydrocarbons when passing methanol over zeolite Y suggests that our previous observation of these hydrocarbons when oxidizing methane over RuPC/Y (Quarterly Report 3, PSR 8) could be due to the activity of the zeolite on product methanol, rather than ligand decomposition as we suggested previously. Such methane dehydrogenation activity, even in the presence of oxygen, is unprecedented at these low temperatures (see Table 4).

Table 5

DECOMPOSITION OF METHANOL ON CATALYST SUPPORTS^a

Catalysts	Temp. (°C)	%Methanol Decomp	%Selectivity ^b				
			CO ₂	C ₁	C ₂	C ₃	C ₄
none	300	0.04	0.0	100.0	0.0	0.0	0.0
	375	1.80	26.5	68.6	2.9	2.0	0.0
Zeolite Y	300	0.11	33.3	66.7	0.0	0.0	0.0
	375	8.42	15.3	31.3	7.9	18.8	26.3
MgO	375	12.20	73.4	26.0	0.04	0.09	0.48
MgO + O ₂ ^c	375	77.91	96.4	3.2	0.18	0.12	0.08

^aConditions: Pressure = 1 atm, Flow rate = 100ml/min., He:CH₃OH = 10.

^bSelectivity was calculated based on the carbon number of the hydrocarbons.

^cHe:O₂:CH₃OH = 8:1:1.

FUTURE WORK

Our studies of methane oxidation suggest many possibilities for further investigation. Our results with the PdTSPC/MgO system show that this catalyst is active at much lower temperatures than other methane oxidative dimerization catalysts. Other metals in a similar environment are relatively inactive; we therefore intend to synthesize other Pd

phthalocyanines, support them on MgO, and examine their reactivity in order to find out how wide-spread this reactivity is. Another potential direction is the synthesis of new TPP derivatives such as the one in which the protons of the phenyl rings are replaced by fluorines (called PFTPP). These are also known homogeneous hydrocarbon oxidation catalysts; in addition, they are stable to higher temperatures than the underivatized TPP complexes. We also need to reexamine the reactivity of the RuPC/Y system and determine whether the hydrocarbons observed previously arise from ligand decomposition or secondary reactions of methanol.

The results in Table 5 show that the support used can be very active in promoting secondary reactions of the primary initial product methanol. Since both acidic and basic supports are active in the decomposition of methanol, a neutral support may catalyze fewer secondary reactions, so that a greater yield of methanol can be observed. One such neutral support is molecular sieve carbon. Other possibilities are zeolites with very high silica/alumina ratios, or aluminophosphates. We have ordered some molecular sieve carbon, and will anchor some of the complexes we have previously examined on this support.

Our results from previous quarters show that the mixed metal FeRu_3 clusters are more active for methane dehydrogenation at lower temperatures than the pure ruthenium clusters. We plan to study other mixed metal systems; for example, Ru_2Fe_2 , Ru_2Os_2 or Re_2Ru_2 cluster.^{37,38} Both osmium and rhenium compounds have displayed activity for hydrocarbon activation in homogeneous systems. Some of the earlier clusters we have examined will be reexamined on molecular sieve carbon support, so that we can compare the effect of support acidity.

In addition to synthesizing new catalysts for methane dehydrogenation, we intend to examine the effects of changing the composition of the gas stream. One means of doing this is by removing the hydrogen byproduct from the reaction very quickly by using a hydrogen selective membrane. Our previous attempts at this suffered from the fragility of

the membrane. Our new Pd/Ag membrane, into which a spring has been inserted to reinforce the tubing, has now arrived. We can thus extend this membrane out of the hot zone, and therefore plan to incorporate it into our reactor setup using helium flow rather than vacuum to remove the hydrogen. We also intend to vary the composition of the gas being fed into the reactor. Raising the percentage of methane in the feed gas should lead to a higher yield of coupling products, since the larger concentration of methane would be a better trap for reactive intermediates than helium. Other hydrocarbons could act as initiators for the methane dehydrogenation.

In analyzing the GC results from our methane dehydrogenation studies, we have not achieved a carbon balance. Elemental analyses of the catalysts after reaction show that the percentage of carbon in the samples have risen dramatically, which implies coke formation. Thus we will be analyzing the samples for coke formation by doing carbon titrations. Another possibility is that the C_6 peak in the GC contains higher hydrocarbons, and so we are underestimating the amount of carbon in these products by assuming it is all C_6 . Analysis of such hydrocarbons in our current reactor-GC setup would involve the addition of a new column and new valving. We have begun to determine the most effective way to incorporate these additions into our system.

EXPERIMENTAL DETAILS

Preparation of Tetrasulfophthalocyanine (TSPC) Complexes:

The procedure is adapted from that reported by Busch and Weber.³⁹ A mixture of the monosodium salt of 4-sulfophthalic acid (0.2 mol), urea (1.2 mol), ammonium chloride (0.2 mol), ammonium molybdate (0.001 mol), nitrobenzene (100 mL), and the appropriate metal compound (0.06 mole $CoCl_2$, $FeCl_2$, $CuCl_2$, $MnSO_4$, $Ru_3(CO)_{12}$, or $Mo(CO)_6$) is added to a 500 mL, three-necked flask fitted with a reflux condensor and a mechanical stirrer. The mixture is heated slowly to 150°C for 0.5 h with continuous stirring or until gas evolution ceases. The temperature is

then raised to 180°C and maintained at this level for 5 h. After cooling, the solid is filtered, washed with 500 mL of methanol and added to 1 L of 1 N HCl. The slurry is heated to reflux for 0.5 h. This solid was filtered off, washed with 200 mL water and dissolved in 1 L of 0.1 N NaOH solution. The solution is then heated at 80°C for 3 h while sodium chloride (300 g) is added slowly. The sodium salt of the TSPC complex precipitated on cooling and after isolation is redissolved in water (1 L). This solution is acidified to pH 2 with 2 N HCl. The precipitate is filtered and dried under vacuum at 80°C overnight to yield the acidic form of the TSPC complex.

Preparation of Magnesium Oxide Supported TSPC Complexes:

The metal TSPC complex (0.5 g) is dissolved in DMF (500 mL), then added to MgO powder (10 g) and stirred for 2 h. After washing with DMF and acetone, the catalysts are dried at 60°C under vacuum overnight.

Testing of Methanol Decomposition:

The reactor system used for testing methane oxidation catalysts has been modified for the introduction of liquid reagents by adding a length of 1/16" s.s. tubing to the inlet of the reactor. Methanol is fed into the reactor (a 3/8" s.s. tube) via a HPLC pump. Helium gas is added to dilute and carry the methanol through the reactor to the GC. The tubing which connects the reactor outlet and the GC is heated to 110°C to minimize condensation. Methanol decomposition was tested on an empty reactor, MgO (2 g), and Na-Y zeolite (2 g).

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