

PARTIAL OXIDATION OF METHANE USING SUPPORTED PORPHYRIN  
AND PHTHALOCYANINE COMPLEXES

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ABSTRACT

The catalytic oxidation of methane with molecular oxygen was investigated in a fixed-bed flow reactor with various anchored metal phthalocyanine (PC) and porphyrins (TPP) as the catalysts. These support organometallic species were stable at temperatures as high as 400°C. Methanol was formed from zeolite encaged RuPC, CoTPP, and MnTPP at 375°C. In contrast, a PdPC complex attached to magnesia produced ethane rather than methanol. The other surface-supported catalysts gave carbon dioxide and water as the sole observable products (by GC).

INTRODUCTION

Conversion of methane to useful chemicals by partial oxidation and oxidative dehydrogenation has received the attention of many researchers.<sup>1</sup> Our first approach to the goal of selective partial oxidation of methane was to synthesize zeolite encapsulated porphyrin and phthalocyanine complexes that mimic the oxygenase enzyme: Cytochrome P-450.<sup>2-5</sup> Porphyrins and phthalocyanines are potent oxidants that also allow 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.

Our second approach to stabilize the phthalocyanine complex is by anchoring the complex on the surface of a support. Magnesium oxide is

known to generate methyl radicals from methane,<sup>6</sup> lithium promoted MgO has shown high selectivity to C<sub>2</sub> hydrocarbons on methane oxidation.<sup>8,9</sup> The metal oxo intermediate generated from the phthalocyanine and oxygen should react with methyl radicals faster than with methane. We prepared magnesium oxide supported catalysts by reacting the basic support with the acid form of tetrasulfophtha-locyanine (TSPC) complexes. The TSPC complexes were anchored to the MgO surface by ionic interaction between the sulfonate groups of the metal complex and the basic sites of MgO.

## EXPERIMENTAL DETAILS

### Preparation of Metal Ion Exchanged Zeolite

To a slurry of 500 g zeolite (LZ-Y52, Unioncarbide) and water (500 mL), a 1M aqueous solution of metal salt (500 mL, FeCl<sub>2</sub>, CoCl<sub>2</sub>, MnSO<sub>4</sub>, or Ru(DMSO)<sub>2</sub>Cl<sub>2</sub>) was added dropwise. The zeolite slurry was stirred at a constant speed. The total addition time was approximately 1 h. The mixture was allowed to stir for 24 h. The exchanged powder was filtered, washed with water until the washing were free of chloride or sulfate and then dried at 150°C under vacuum for 48 h. Elemental analysis of Co-zeolite: C, 0.27; H, 0.91; Co, 4.76; Fe-zeolite: C, 0.26; H, 1.20; Fe, 4.89; Ru-zeolite: C, 1.16; H, 1.08, Ru, 0.95.

### Preparation of zeolite encapsulated metallophthalocyanine

Metal exchanged zeolite (100 g) and 8 equivalent of 1,2-dicyanobenzene were added to 200 mL of nitrobenzene in a round bottom flask fitted with a reflux condenser and a mechanical stirrer. The mixture was heated to 180°C for 4 h under nitrogen until the solution changed color (dark green for Fe, dark blue for Co, brown for Mn and Ru). The zeolite was filtered, washed with methanol to remove nitrobenzene, and Soxhlet extracted with pyridine until the solution was clear. Excess pyridine was removed by Soxhlet extraction with methanol. The zeolite powder was then boiled in a 1 M solution of NaCl (reverse metal exchange) for 4 h, washed with water and acetone. The product was dried at 150°C under vacuum for 24 h.

### Preparation of zeolite encapsulated tetraphenylporphyrin

Zeolite powder (200 g) was added to 1.8 L of acetic acid in a 2 L round bottom flask equipped with mechanical stirrer and an addition funnel which contained 46.5 mL pyrrol and 66.5 mL of benzaldehyde. The acetic acid was heated to boil. The pyrrol and benzaldehyde were added slowly. The reaction mixture was boiled for 0.5 h under air. The dark purple solid was filtered while the solution was still warm. It was then washed with large amount of acetone until the washing was colorless. The product was dried at 150°C under vacuum for 24 h.

### Metal insertion of tetraphenylporphyrin in zeolite

A mixture of TPP zeolite (50 g) and metal salt (0.12 mole of  $\text{CoCl}_2$ ,  $\text{FeCl}_2$ ,  $\text{MnSO}_4$ , or  $\text{Ru}_3(\text{CO})_{12}$ ) was added to 200 mL of dimethyl sulfoxide in a three necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, and a gas inlet adaptor. The reaction mixture was heated to reflux for 3 h. The product was washed with water and methanol. Excess metal salt was removed by boiling in a 1 M aqueous solution of NaCl for 2 h. The product was washed again with water and methanol and then dried at 150°C for 24 h.

### Preparation of magnesia supported tetrasulfothalocyanines

The tetrasulphthalocyanine complexes were prepared via the reaction of monosodium salt of 4-sulfophthalic acid, urea, and metal salt in the presence of catalytic amounts of ammonium molybdate, and ammonium chloride at 180°C. The acid form of the complexes were obtained by acidification of the aqueous solutions with 2 N HCl. The resulting metal complex (0.5 g) was then dissolved in DMF (500 mL), added to MgO powder (10 g), and stirred for 2 h. After washing with DMF and acetone, the catalysts were dried at 60° under vacuum overnight. Five catalysts: PdTSPCMgO, FeTSPCMgO, CuTSPCMgO, RuTSPCMgO, CoTSPCMgO, were prepared by this method.

### General procedure for testing methane oxidation catalysts

The catalyst (3 g) was loaded into a stainless steel reactor (3/8" OD). The reactor was connected to the reactor system and purged with helium for 15 min. It was heated to 200°C under a slow flow of hydrogen for 2 h. Methane (10.3% in helium) and oxygen (5.2% in helium) were introduced to the reactor and the temperature was increased to 300°C or higher. Methane and oxygen were individually controlled by mass flow controllers. The reactor pressure was set at 50 psig via a back pressure regulator. A thermocouple was immersed in the catalyst bed and connected to a temperature controller that controls the furnace. The outlet gases were fed to a GC sampling valve through heated stainless steel tubing (110°C).

### RESULTS AND DISCUSSION

Phthalocyanine complexes are synthesized within the zeolite pore by first exchanging the metal ion into the pore, followed by template condensation.<sup>10</sup> We used Na-Y zeolite because it has large pores that allows the phthalocyanine complexes to fit in and contains exchangeable ions. Some of the phthalocyanines that absorbed on the zeolite surface were removed by extraction with pyridine and acetone. Excess metal ions were then back exchanged with sodium ions. Surface reflectance UV-Vis and FT-IR of the non-extracted catalysts evidenced the presence of phthalocyanine.

The zeolite encapsulated metalloporphyrins was synthesized by a modified method. The metal free ligand was first synthesized inside the zeolite cage by refluxing benzaldehyde, pyrrol, and the Na-Y zeolite (without metal exchange) in acetic acid. The surface attached porphyrin was extracted with methanol. The washings contain tetraphenylporphyrin as indicated by its UV-Vis spectrum.

The desired metal ion was inserted into the porphyrin by boiling the metal salt and the zeolite containing the porphyrin in dimethyl-

sulfoxide solution. The product was washed with water and then Soxhlet extracted with methanol to remove surface-bound TPP complex. Uncomplexed metal ions are removed by reverse ion-exchange with sodium chloride. However, the excess iron ions were not exchangeable by sodium ions and we have not attempted to remove the excess iron by another method. The FePCZL and the ReTPPZL thus contained excess iron ions. The metal loading (by weight) and the percent of super cages occupied by the metal complexes (calculated based on the results from elemental analyses) are listed in Table 1.

Table 1

METAL AND COMPLEX LOADING OF ZEOLITE ENCAPSULATED COMPLEXES

<u>Catalyst</u> <sup>a</sup>	<u>Wt. % metal Loading</u>	<u>% Supercages Occupied</u>
CoPCZL	1.53	60
FePCZL	4.15 <sup>b</sup>	50
RuPCZL	0.97	20
MnPCZL	1.62	68
CoTPPZL	0.15	5
FeTPPZL	4.04 <sup>b</sup>	8
RuTPPZL	0.13	2.5
MnTPPZL	0.12	4.3

<sup>a</sup>Pc = phthalocyanine, TPP = Tetraphenylporphyrin, ZL = zeolite.

<sup>b</sup>The iron complexes contained excess iron ions which can not be exchanged by sodium ions.

These zeolite catalysts were tested for methane oxidation at 375°C under 50 psig pressure. The results are averaged from data taken during the 15 to 20 h of the runs and are summarized in table 2. Three catalysts including RuPcZL, CoTPPZL, and MnTPPZL showed some reactivity toward the formation of methanol. As shown in table 5, the RuPcZL gave the highest selectivity of methanol. The methane conversions were generally below 10%. Carbon dioxide and water were always the major products.

Three control experiments were run using the blank zeolite, ruthenium exchanged zeolite (with triruthenium dodecacarbonyl), and ruthenium tetracarboxyphthalocyanine. The blank zeolite gave essentially no reactivity toward methane oxidation. Less than 0.5% of methane was oxidized to carbon dioxide. The ruthenium zeolite produced hydrogen, carbon dioxide and water with approximate 16% methane conversion. The RuTPPZL and FePcZL also gave hydrogen which suggest that these two catalysts behaved like the simple metal exchanged zeolite, because the excess metal ion in these two catalysts was not removed by the reverse ion exchange process. The productions of hydrogen were due to the catalytic ability of the zeolite adsorbed metal particles.

Table 2

ACTIVITY OF METHANE OXIDATION CATALYSTS

Catalyst	% Conv. of CH <sub>4</sub>	H <sub>2</sub>	% Selectivity of		
			CO <sub>2</sub>	H <sub>2</sub> O	CH <sub>3</sub> OH
Zeolite	0.5	---	100	---	---
RuZL	15.9	45	100	100	---
CoPcZL	6.3	---	100	100	---
FePcZL	18.2	1.2	100	42	---
RuPcZL	4.8	---	87	1	11.3
MnPcZL	9.6	---	80	65	---
CoTPPZL	1.9	---	94	120	5.8
FeTPPZL	1.9	---	100	73	---
RuTPPZL	8.4	50	99	146	---
MnTPPZL	1.8	---	95	126	3.5

Reaction conditions: Temperature=375C, Pressure=50psig, CH<sub>4</sub>/O<sub>2</sub>=4, GHSV=2600 h<sup>-1</sup>.

Some of the catalysts were also tested at higher temperature under the same condition. The results were summarized in Table 3. Methane conversions were generally increased at higher temperature. Again, only

RuPcZL and CoTPPZL showed some activity toward methanol formation, but the yields were significantly decreased. These results indicated that the metal complexes decomposed at high temperature and therefore lost their activity. The characteristic blue green color of the phthalocyanines and the purple color of the porphyrins disappeared after the high temperature reactions. The decomposition of catalysts were confirmed by elemental analyses.

Table 3

ACTIVITY OF METHANE OXIDATION CATALYST AT HIGH TEMPERATURE

Catalyst	Temp. (°C)	% Conversion		% Selectivity			
		CH <sub>4</sub>	O <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	CH <sub>3</sub> OH
RuZL	500	20.8	99.0	110.0	89.3	---	---
FePcZL	500	22.7	87.2	15.9	100.0	45.0	---
RuPcZL	450	9.0	99.6	---	96.7	0.5	3.3
CoTPPZL	450	3.3	56.1	---	98.0	126.2	2.0
FeTPPZL	450	6.1	32.8	---	100.0	65.1	---

Reaction conditions: Pressure=50 psig, CH<sub>4</sub>/O<sub>2</sub> = 4, GHSV = 2600 h<sup>-1</sup>.

It has been noted that high levels of complex loading results in blocking the access of substrate to the metal center.<sup>11</sup> The zeolite encapsulated phthalocyanines prepared in this work contained relatively high complex loading. About half of the super cages in the zeolite were filled with metal complex in the CoPCZL, FePCZL, and MnPCZL. The RuPCZL was the only catalyst that showed activity and it contained less metal complex than the others. We are not certain whether the lack of catalytic activity was due to the accessibility of methane to the active site of the catalyst or was truly an inactive metal complex since methane is a rather small molecule. In contrast, the TPP analog of RuPCZL was not active in converting methane to methanol but the CoTPPZL

and the MnTPPZL were active. Since all the zeolite encapsulated TPP complexes contained low complex loading, the nature of the metal complex should be responsible for the catalytic activity.

We tested four metal complexes of tetrasulfophthalocyanine supported on magnesium oxide (Pd, Fe, Ru, Cu). The metal loading and complex loading are listed in Table 4. Interestingly, the palladium catalyst (PdTSPCMgO) produced ethane from the oxidation of methane at 375°C instead of methanol (Table 5). Although the selectivity was low (2.8%), oxidative coupling of methane to ethane at such low temperature is unusual. Increasing the reaction temperature to 400°C, increased methane conversion and decreased ethane selectivity. Further increases of the temperature to 450°C decomposed the complex. All other catalysts tested gave only products of complete oxidation, ie. CO<sub>2</sub> and H<sub>2</sub>O.

Table 4

METAL LOADING AND COMPLEX LOADING OF THE MAGNESIUM OXIDE SUPPORTED CATALYSTS

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

<sup>a</sup>Based on elemental analysis.

<sup>b</sup>Mole of complex were calculated based on the carbon weight from the elemental analyses.

Table 5

ACTIVITY OF MgO SUPPORTED METHANE OXIDATION CATALYSTS<sup>a</sup>

Catalysts	Temp. (°C)	%Conversion of Methane	%Selectivity <sup>b</sup>	
			CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>
PdTSPCMgO	375	1.4	97.2	2.8
	400	2.6	97.8	2.2
	450	5.7	99.7	0.3

<sup>a</sup>Condition: Pressure = 1 atm, CH<sub>4</sub>/O<sub>2</sub> = 10, GHSV = 5000 h<sup>-1</sup>.

<sup>b</sup>Selectivity was calculated based on carbon number.

## CONCLUSION

To the best of our knowledge, this is the first observation of methanol production from partial oxidation of methane using cytochrome-P450 mimic. Encapsulating the porphyrin and phthalocyanine complexes inside the zeolite cages precludes the intermolecular reactions which leads to the problem of catalyst deactivation. Anchoring the metal complexes on the support surface also prevents such bimolecular self destruction. Oxidative coupling of methane is usually observed at temperature much higher ( $>700^{\circ}\text{C}$ ) than what we observed for PdTSPCMgO ( $375^{\circ}\text{C}$ ). Many questions remained to be answered including improving product selectivity.

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